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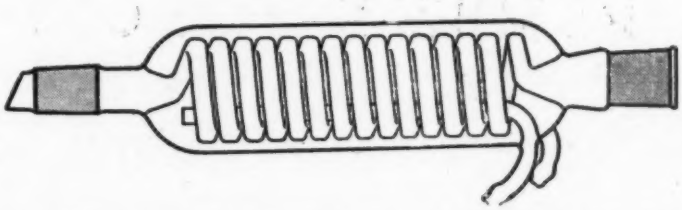

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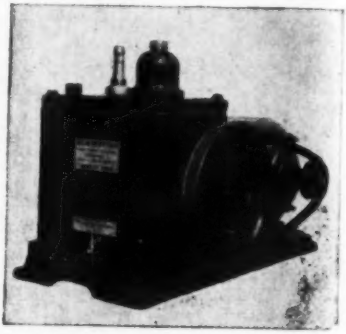

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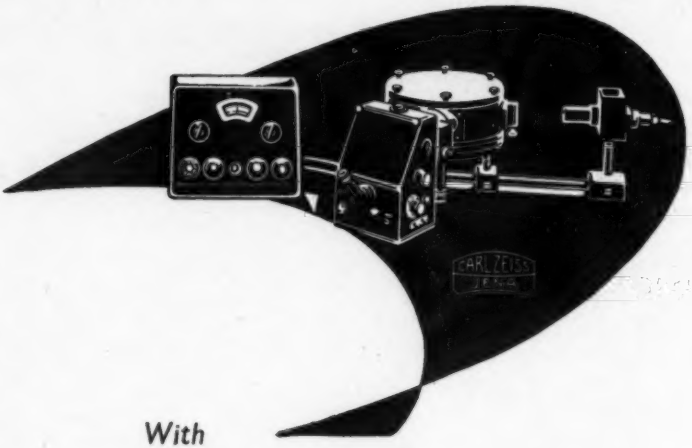

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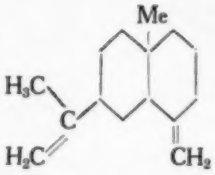
[Jour. Indian Chem. Soc., Vol. 37, No. 11, 1960]

AN ATTEMPT TOWARDS THE SYNTHESIS OF β-SELINENE*

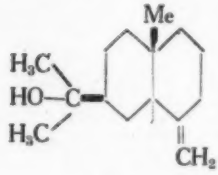
BY D. K. BANERJEE AND P. S. HALWE

An attempt to obtain β-selinene (I) by the pyrolysis of 4-acetoxymethyl-6-(α-acetoxymethylethyl)-9-methyldecalin (IV) has been described. A synthesis of (IV) has been reported, and proof of the structure of the important intermediate, methyl 6-methyl-6-ethoxycarbonylcyclohexanone-3-α-propionate, has been provided.

The sesquiterpene hydrocarbon, selinene, was first isolated by Ciamician and Silber (*Ber.*, 1897, **30,** 496) from the fruit of *Apium graveolens*, and was assigned the structure (I) (Simonsen, 'The Terpenes', Vol. III, Cambridge University Press, p. 32, 1952). The relationship of eudesmol to selinene was established by Ruzicka *et al.* (*Helv. Chim. Acta*, 1931, **14,** 1178) and eudesmol was assigned the absolute configuration (II) by correlating it to the steroids of known absolute configuration (Woodward *et al.*, *J. Amer. Chem. Soc.*, 1954, **76,** 313).

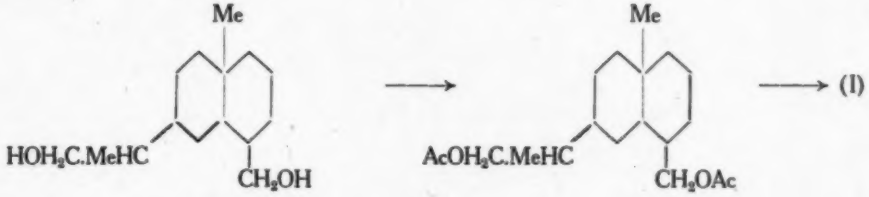


(I)



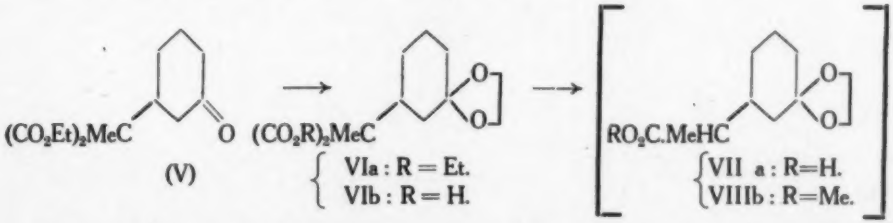
(II)

The present investigation was undertaken with a view to synthesising β-selinene. It appeared to us that the diol (III) through pyrolysis of its acetate (IV) (Bailey *et al.*, *ibid.*, 1953, **75,** 4780; 1954, **76,** 2251; 1955, **77,** 75) might yield a bicyclic system with the characteristic features of β-selinene (I).

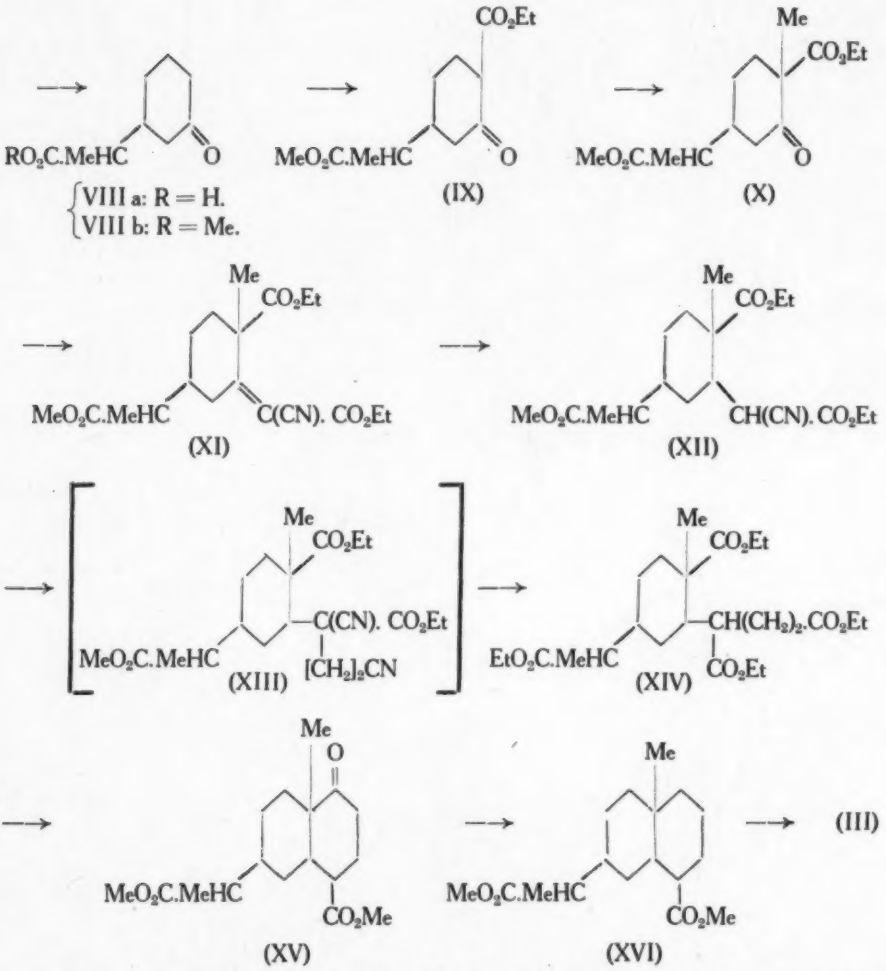


(III) (IV)

The scheme for the synthesis of the diol (III) has been outlined below.



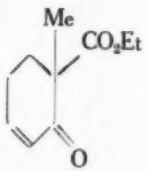
* This paper was presented at the symposium on Terpenoids, held under the auspices of the Indian Chemical Society in Calcutta on March 15, 1958.



We first attempted to prepare ethyl *cyclo*hexanone-3-methylmalonate (V) by methylation of ethyl *cyclo*hexanone-3-malonate using sodium methoxide, but only a very poor yield of the methylated product could be obtained due to retrogression of the Michael reaction. Condensation of Δ^2-*cyclo*hexenone with diethyl methylmalonate (2 moles) in presence of sodium methoxide (1 mole) in methanol (Masanao Matasui *et al.*, *Bull. Chem. Soc. Japan*, 1954, **27,** 7) afforded only 25% yield of the adduct (V), while condensation in presence of 1/6 mole of sodium ethoxide in ether (Michael and Ross, *J. Amer. Chem. Soc.*, 1930, **52,** 4598) furnished ethyl *cyclo*hexanone-3-methylmalonate (V) in 74% yield. During the aforementioned Michael reaction a small quantity of an alkali-soluble product (*ca.* 1%), which exhibited violet colour with ethanolic ferric chloride, was also obtained, but not further investigated. Hydrolysis of the keto-malonic ester (V) with hydrochloric acid or sulphuric acid or methanolic alkali afforded only 25-30% yield of *cyclo*hexanone-3-α-propionic acid (VIIIa). The keto group of (V) was next protected by preparing ethyl 1-ethylenedioxy*cyclo*hexane-3-methylmalonate (VIa). The latter was saponified by refluxing with an excess

of methanolic alkali followed by careful acidification with dilute hydrochloric acid to furnish the di-acid (VIb), which in the crude state was decarboxylated and esterified with diazomethane, followed by regeneration of the ketone (VIIIb) from its ketal (VIIb) to obtain methyl *cyclo*hexanone-3-α-propionate (VIIIb) in 52% yield. Prior regeneration of the keto-acid (VIIIa) from (VIIa), followed by esterification, however, increased the yield to 68%. Methyl 6-ethoxycarbonyl*cyclo*hexanone-3-α-propionate (IX) was obtained by condensing methyl *cyclo*hexanone-3-α-propionate (VIIIb) with diethyl oxalate in an ethanolic solution of sodium ethoxide, followed by pyrolysis of the resulting glyoxalate, in 61% yield. Methylation of the aforementioned β-keto-ester (IX) using sodium dust and methyl iodide in benzene (Linstead and Millidge, *J. Chem. Soc.*, 1936, 478) furnished methyl 6-methyl-6-ethoxycarbonyl*cyclo*hexanone-3-α-propionate (X) in 90% yield.

That the condensation of diethyl oxalate with methyl *cyclo*hexanone-3-α-propionate (VIIIb) occurred in the C_6 position and not in the C_2 position was proved by conversion of methyl 6-methyl-6-ethoxycarbonyl*cyclo*hexanone-3-α-propionate (X) into ethyl 6-methyl*cyclo*hexanone-3-α-propionate (XIX) by treating the former with aqueous alkali, followed by esterfication. The melting point of the semicarbazone of (XIX) remained undepressed on admixture with the semicarbazone of an authentic specimen of ethyl 6-methyl*cyclo*hexanone-3-α-propionate. An authentic sample of (XIX) was prepared by a slight modification of the procedure of Mukherjee (this *Journal*, 1948, **25**, 155) (vide Experimental).



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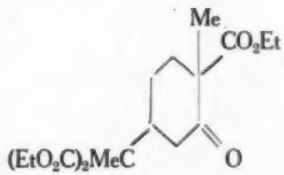

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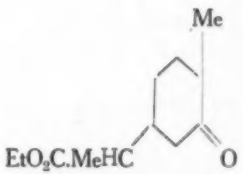

(XIX)

Condensation of methyl 6-methyl-6-ethoxycarbonyl*cyclo*hexanone-3-α-propionate (X) with ethyl cyanoacetate, using ammonium acetate and glacial acetic acid, was carried out by following essentially the conditions of Banerjee and Shafer (*J. Amer. Chem. Soc.*, 1950, **72**, 1931) to obtain ethyl 6-ethoxycarbonyl-6-methyl-3-(α-methoxycarbonylethyl)-*cyclo*hexylidenecyanoacetate (XI) in 54% yield. The unsaturated cyano-ester (XI) was reduced with palladium charcoal as catalyst under pressure. The addition of acrylonitrile to the aforementioned cyano-ester (XII) was carried out in presence of 'Triton B' in dioxane to furnish ethyl 6-methyl-6-ethoxycarbonyl-3-(α-methoxycarbonylethyl)-*cyclo*hexyl-(β-cyanoethyl)-cyanoacetate in 95% yield (XIII). The dicyano-ester (XIII) was hydrolysed and esterified to yield 6-methyl-6-ethoxycarbonyl-3-(α-ethoxycarbonylethyl)-1-(αγ-diethoxycarbonylpropyl)-*cyclo*hexane (XIV) in 54% yield. Dieckmann cyclisation of the tetra-ester (XIV) afforded 1-keto-2:4-diethoxycarbonyl-6-(α-methoxycarbonylethyl)-9-methyldecalin, which was hydrolysed and decarboxylated by refluxing with dilute hydrochloric acid and subsequently esterified with diazomethane to yield 1-keto-4-methoxycarbonyl-6-(α-methoxycarbonylethyl)-9-methyldecalin (XV) (overall yield 58%). The decalone (XV) was reduced by Clemmensen's method and esterified with diazomethane to furnish 4-methoxycarbonyl-6-(α-methoxycarbonylethyl)-9-methyldecalin (XVI) in 70% yield. The di-ester (XVI) was next reduced with lithium aluminium hydride to afford 4-hydroxymethyl-6-(α-hydroxymethylethyl)-9-methyldecalin (III) in 90% yield. The diacetyl derivative (IV) was prepared by heating the diol (III) with acetic anhydride and pyridine in 85% yield. The pyrolysis of 4-acetoxymethyl-6-(α-acetoxymethylethyl)-9-methyldecalin (IV) according to the procedure

of Bailey (*loc. cit.*, 1953) provided a hydrocarbon in 29% yield, the analysis of which fits $C_{15}H_{24}$ (λ_{max}^{EtOH} 224 mμ, log ε 4.2). The hydrocarbon has the characteristic bands in I.R. region at 886 cm^{-1} $\left(\begin{matrix}R_1\\R_2\end{matrix}\!\!>\!C{=}CH_2\right)$ (Thompson and Whiffen, *J. Chem. Soc.*, 1948, 1412) and 1625cm^{-1}

$$\left(\diagdown C=\overset{H}{\overset{|}{C}}-\overset{|}{C}=C-\right)$$

(Naves, *Bull. Soc. Chim.*, 1956, 292). The synthetic hydrocarbon appears to be a mixture of isomers of selinene.

EXPERIMENTAL*

Δ^2-cyclo*Hexenone* was prepared from 2-chloro*cyclo*hexanone ("Organic Syntheses", 1945, Vol. XXV, p. 22, John Wiley & Sons, New York) according to the procedure of Wanzlick (*Ber.*, 1955, **88,** 69) in 59% yield.

Ethyl cyclo*Hexanone*-3-*malonate* was obtained according to the procedure of Bartlett and Woods (*J. Amer. Chem. Soc.*, 1940, **62,** 2933), b.p. 145-47°/2 mm, $n_D^{25.2}$ 1.4613, yield 81%.

Ethyl cyclo*Hexanone*-3-*methylmalonate* (V).—To a solution of sodium (1.8 g., 1/6 mole) in anhydrous ethanol (4 c.c.) and dry ether (200 c.c.) diethyl methylmalonate (85 g.) ("Organic Syntheses", Vol. XVII, 1937, p. 54, John Wiley & Sons, New York) was added, followed by *cyclo*hexenone (45 g.) in dry ether (100 c.c.), when a vigorous reaction ensued and the ether started refluxing. The reaction mixture was refluxed for 5 hours on a water bath. After cooling, acetic acid (5 c.c.) in water (50 c.c.) was added to it. The ethereal layer was first washed with sodium bicarbonate solution and then extracted with 2% ice-cold alkali, and finally washed with water. After removing the solvent the residue was distilled to provide unchanged *cyclo*hexenone and diethyl methylmalonate (34 g.), b.p. up to 95°/2 mm, and ethyl *cyclo*hexanone-3-methylmalonate, b.p. 158-60°/1-2 mm, n_D^{24} 1.4629; yield 93.55 g. (74%). (Found : C, 61.76; H, 8.34. $C_{14}H_{22}O_5$ requires C, 62.10; H, 8.15%).

The *semicarbazone*, after crystallisation from ethanol, melted at 149-50°. (Found : N, 12.81. $C_{15}H_{25}O_5N_3$ requires N, 12.84%).

The alkaline extract was acidified with cold HCl (dil.) and extracted with ether. After removing the solvent the residue was distilled, b.p. 52°/2 mm, yield 1 g. The distillate showed violet colour with alcoholic ferric chloride, but the product was not identified.

Ethyl 1-*Ethylenedioxy*cyclo*hexane*-3-*methylmalonate* (VIa).—A mixture of ethyl *cyclo*hexanone-3-methylmalonate (154 g.), ethylene glycol (45 c.c.), *p*-toluenesulphonic acid (100 mg.), and benzene (300 c.c.) was refluxed in a flask fitted with a continuous water separator. The refluxing was continued till the water had ceased to separate (*ca.* 48 hours). The cooled reaction mixture was washed with sodium bicarbonate solution and water. After removing the solvent the product was distilled, b.p. 168-69°/2 mm, n_D^{26} 1.4672; yield 176 g. (98%). (Found : C, 60.70; H, 8.24. $C_{16}H_{26}O_6$ requires C, 61.15; H, 8.28%).

Methyl cyclo*Hexanone*-3-α-*propionate* (VIIIb).—(*a*). Ethyl 1-ethylenedioxy*cyclo*hexane-3-methylmalonate (60 g.) was refluxed for 4 hours with KOH (33 g.) in water (25 c.c.), and methanol

* All recorded m.p. and b.p.'s are uncorrected.

(325 c.c.). The methanol was distilled off and iced water was added to the product. The solution was made just acidic to litmus with ice-cold 6*N*-HCl and extracted with ether. The ether extract was washed with water and dried over sodium sulphate. After removing the solvent the crude malonic acid derivative (VIb) was decarboxylated by heating with glass powder at 160° in an oil bath. After cooling, the acid (VIIa) was shaken with HCl (50 c.c., 10%) for 30 mins. with slight warming on the water bath (*ca.* 50-60°). The deketalised acid was taken in ether and the aqueous layer extracted with ether. The combined ether layer was washed with water. The crude *cyclo*hexanone-3-α-propionic acid was esterified with diazomethane, prepared from 42 g. of nitrosomethylurea, in the usual way and purified by distillation, b.p. 109°/2 mm, n_D^{23} 1.4649; yield 25 g. (68%). (Found : C, 65.56; H, 8.61. $C_{10}H_{16}O_3$ requires C, 65.22; H, 8.69%).

The *semicarbazone* crystallised from ethanol, m.p. 158-59°. (Found : N, 17.56. $C_{11}H_{19}O_3N_3$ requires N, 17.43%).

A small quantity of *cyclo*hexanone-3-α-propionic acid was purified by short-path distillation, bath temperature 145-47°/1 mm, n_D^{25} 1.4838. (Found : C, 63.06; H, 8.37. $C_9H_{14}O_3$ requires C, 63.53; H, 8.23%).

(*b*). A mixture of ethyl *cyclo*hexanone-3-methylmalonate (11 g.), KOH (7 g.) in water (6 c.c.), and methanol (50 c.c.) was refluxed for 2 hours on a water bath. The methanol was removed under diminished pressure and the product was diluted with water. The cooled reaction mixture was acidified with H_2SO_4 (dil.) and extracted several times with ether. The *cyclo*hexanone-3-methylmalonic acid, obtained after removal of the solvent, was decarboxylated by heating with glass powder at 160° in a preheated oil bath to yield *cyclo*hexanone-3-α-propionic acid, which was purified by short-path distillation, bath temperature 143-45°/2 mm, yield 1.7 g. (25%).

(*c*). A mixture of ethyl *cyclo*hexanone-3-methylmalonate (12.36 g.), HCl (40 c.c.), and water (40 c.c.) was refluxed for 24 hours in an oil bath. After cooling, the keto-acid was extracted with ether, and after removing the solvent the residue was purified by short-path distillation, bath-temperature 140-42°/1-2 mm, yield 2.17 g. (28%).

Methyl 6-Ethoxycarbonylcyclohexanone-3-α-propionate (IX).—To sodium dust (3 g.) under dry ether (60 c.c.), cooled in a freezing mixture (ice and salt), was added dropwise dry ethanol (6 g.), and the mixture was left overnight. Ethyl oxalate (21 g.) was then added in the cold (0°). The reaction mixture on being kept aside for 3 hours was cooled in a freezing mixture (ice and salt) and methyl *cyclo*hexanone-3-α-propionate (23.5 g.) was slowly added with continuous shaking. The reaction mixture was kept at 0° for 48 hours, when it turned deep red. It was diluted with iced water and the ether layer was extracted with 2% ice-cold alkali. The combined aqueous layer was acidified with ice-cold HCl (dil.) and extracted with ether; the ether extract was washed with water and dried over calcium chloride. After removing the solvent, the glyoxalate was heated with glass powder at 160-65° in a preheated oil bath till evolution of carbon monoxide had ceased; the product was distilled to furnish methyl 6-ethoxycarbonyl*cyclo*hexanone-3-α-propionate, b.p. 148-50°/1 mm, n_D^{23} 1.4762; yield 20 g. (61%). (Found : C, 61.08; H, 7.98. $C_{13}H_{20}O_5$ requires C, 60.94; H, 7.81%).

Methyl 6-Methyl-6-ethoxycarbonylcyclohexanone-3-α-propionate (X).—The preceding ester (IX) (19.16 g.) was added dropwise to sodium dust (1.8 g.) in dry benzene (50 c.c.), cooled in ice and water, and allowed to stand overnight. Methyl iodide (20 c.c.) was added and the reaction mixture was refluxed for 4 hours. A further quantity of methyl iodide (10 c.c.) was added and the refluxing continued for 2 hours more. Water was added to the cooled reaction mixture and the benzene

layer washed with water. After removing the solvent the product was distilled, b.p. 155-57°/1-2 mm, $n_D^{22.5}$ 1.4651; yield 18.34 g. (90%). (Found : C, 62.22; H, 8.73. $C_{14}H_{22}O_5$ requires C, 62.22; H, 8.15%). The product did not exhibit any colour with ethanolic ferric chloride.

Ethyl 6-Methylcyclohexanone-3-α-propionate (XIX).—A mixture of compound (X) (3.4 g.) and a solution of KOH (2.4 g.) in water (24 c.c.) was refluxed for 9 hours. The cooled solution was acidified with HCl (dil.) and extracted with ether-benzene. After removing the solvent mixture, the acid was dried in a desiccator. The crude dry keto-acid was refluxed with anhydrous ethanol (25 c.c.) and concentrated sulphuric acid (5 c.c.) for 20 hours. Brine was added to the cooled reaction mixture and extracted with ether-benzene mixture. The extract was washed with sodium bicarbonate solution and water. After removing the solvent the residue was distilled, b.p. 112°/1 mm, n_D^{27} 1.4588; yield 1.93 g. (85%). (Found : C, 67.99, H, 9.51. $C_{12}H_{20}O_3$ requires C, 67.94; H, 9.43%).

The *semicarbazone* crystallised from ethanol, m.p. 169-70°. [(Reported m.p. 156° (Mukherjee, *loc. cit.*) and 169° (Gunstone and Tulloch, *J. Appl. Chem.*, 1954, **4**, 291)]. (Found : N, 15.54. $C_{13}H_{23}O_3N_3$ requires N, 15.61%). This melting point was not depressed on admixture with an authentic sample.

An Authentic Specimen of the Semicarbazone of Ethyl 6-Methylcyclohexanone-3-α-propionate.—6-Ethoxycarbonyl-6-methyl-Δ^2-*cyclo*hexenone was prepared according to the procedure of Mukherjee (*loc. cit.*). The desired product had b.p. 113-16°/11 mm.

To a solution of sodium ethoxide, prepared from sodium (0.15 g.), dry ethanol (1 c.c.), and dry ether (50 c.c.), diethyl methylmalonate (5.5 g.) was added followed by 6-ethoxycarbonyl-6-methyl-Δ^2-*cyclo*hexenone (5.5 g.) in dry ether (25 c.c.). The mixture was refluxed for 6 hours. Acetic acid (1 c.c.) was added to the cooled reaction mixture, and the ether layer was separated and washed with water, 2% alkali, and again with water. After removing the solvent ethyl 6-methyl-6-ethoxycarbonyl*cyclo*hexanone-3-methylmalonate was distilled, b.p. 178-80°/1 mm, yield 7.5 g. (70%). The same compound was previously obtained by Mukherjee (*loc. cit.*) by methylation of ethyl 6-methyl-6-ethoxycarbonyl*cyclo*hexanone-3-malonate.

A mixture of ethyl 6-methyl-6-ethoxycarbonyl*cyclo*hexanone-3-methylmalonate (7.5 g.) and a solution of KOH (8 g.) in water (8 c.c.) was refluxed for 10 hours. The cooled reaction mixture after extraction with ether was acidified with cold HCl (dil.) and then extracted with ether-benzene mixture. The extract was washed with water and the solvent mixture removed. The residue was dried in a desiccator and then refluxed for 16 hours with dry ethanol (25 c.c.) and H_2SO_4 (2 c.c.). The ester was worked up in the usual way to obtain ethyl 6-methyl*cyclo*hexanone-3-α-propionate, b.p. 110°/1-2 mm, n_D^{27} 1.4588 ; yield 1.77 g. (45%).

The *semicarbazone* after crystallisation from ethanol melted at 169-70°.

Ethyl 6-Ethoxycarbonyl-6-methyl-3-(α-methoxycarbonylethyl)-cyclohexylidenecyanoacetate (XI).—A mixture of the ester (X) (37.5 g.), ethyl cyanoacetate (15.9 c.c.), ammonium acetate (6.9 g.), glacial acetic acid (10.5 c.c.), and benzene (38 c.c.) was refluxed in a flask fitted with a continuous water separator till the water had ceased to separate (*ca.* 25 hours). The reaction mixture was cooled and washed 6 times with water. After removing the solvent, the product was distilled to furnish (*i*) ethyl cyanoacetate, 4.6 g., b.p. 75°/1 mm ; (*ii*) a mixture of (*i*) and (*iii*) (18.75 g.), b.p. 148-96° /1mm ; (*iii*) the pure unsaturated cyano-ester (XI), b.p. 200-205°/1 mm, n_D^{28} 1.4791 ; λ_{max}^{EtOH} 235 mμ, log ε 3.94 ; yield 27.35 g. (54%). (Found : N, 3.83. $C_{19}H_{27}O_6N$ requires N, 3.83%).

Ethyl 6-Methyl-6-ethoxycarbonyl-3-(α-methoxycarbonylethyl)-cyclohexylcyanoacetate (XII).—Hydrogenation of the unsaturated cyano-ester (XI) (19 g.) was carried out at an initial pressure of 25 atoms. in the presence of palladised charcoal (5%, 0.3 g.) in purified ethanol (75 c.c.). The reduction was complete in 20 hours. Palladised charcoal was filtered off and the solvent removed. The residue was distilled, b.p. 170-72°/1.6×10^{-2} mm, $n_D^{22.5}$ 1.4741; yield 16.55 g. (89%). (Found: C, 61.93; H, 8.04; N, 3.66. $C_{19}H_{29}O_6N$ requires C, 61.98; H, 7.90; N, 3.81%).

6-Methyl-6-ethoxycarbonyl-3-(α-ethoxycarbonylethyl)-1-(αγ-diethoxycarbonylpropyl)-cyclohexane (XIV).—To an ice-cold solution of the saturated cyano-ester (XII) (10.54 g.) and acrylonitrile (1.6 g.) in dioxane (10 c.c.) was slowly added "Triton B"; the mixture was kept in an ice bath for 1 hour with occasional swirling. The reaction mixture was kept for 7 days at the room temperature, when it turned deep brown. It was then taken up in benzene, washed thoroughly with HCl (dil.), and finally with water. The solvent was thoroughly removed leaving the crude product as a viscous oil, yield 11.5 g. (95%). This product could not be distilled without decomposition and it was not analysed.

The crude dicyano-ester (XIII) (11.51 g.) was refluxed for 60 hours with HCl (conc., 75 c.c.). The mixture was extracted with ether-benzene. The solvent mixture was removed and the crude tetracarboxylic acid (9.12 g.) after drying in *vacuo* was refluxed for 94 hours with a mixture of dry ethanol (100 c.c.) and H_2SO_4 (conc., 18 c.c.). The tetra-ester was worked up in the usual way, b.p. 195-200°/1 mm, yield 6.55 g. (54%). (Found: C, 62.99; H, 8.67. $C_{24}H_{40}O_8$ requires C, 63.13; H, 8.77%).

1-Keto-4-methoxycarbonyl-6-(α-methoxycarbonylethyl)-9-methyldecalin (XV).—To sodium dust (0.62 g.) under benzene (20 c.c.) was added the tetra-ester (XIV) (6.8 g.) through a separatory funnel in an atmosphere of nitrogen. The separatory funnel was then washed down with dry benzene (5 c.c.). The reaction started immediately and the mixture was refluxed for 9 hours. The product was cooled in an ice bath under nitrogen, and to it was added HCl (dil.). The benzene layer was separated and washed with sodium bicarbonate solution and water. The residue obtained after removal of the solvent gave a violet colour with alcoholic ferric chloride. A small portion of this β-keto-ester was purified by short-path distillation, bath temperature 145-50°/1 mm, for analysis. (Found: C, 64.86; H, 8.54. $C_{22}H_{37}O_7$ requires C, 64.39; H, 8.29%).

The aforementioned crude β-keto-ester was refluxed for 24 hours with 15% H_2SO_4 (dil., 50 c.c.). The cooled solution was extracted with ether-benzene. After removal of the solvent mixture the crude keto-acid (4.2 g.) was esterified with diazomethane, prepared from 4 g. of nitrosomethyl urea, to yield 1-keto-4-methoxycarbonyl-6-(α-methoxycarbonylethyl)-9-methyldecalin, b.p. 160-65°/3.2×10^{-2} mm, yield 2.56 g. (58%). (Found: C, 65.70; H, 8.31. $C_{17}H_{26}O_5$ requires C, 65.8; H, 8.38%).

4-Methoxycarbonyl-6-(α-methoxycarbonylethyl)-9-methyldecalin (XVI).—A mixture of the keto-ester (XV) (8 g.), toluene (50 c.c), water (70 c.c.), HCl (conc., 100 c.c.), and acetic acid (10 c.c.) was refluxed for 48 hours with amalgamated zinc (42 g.). Fresh portions of HCl (10 c.c.) were added at intervals of 6 hours. The toluene layer, which was yellow in the beginning, became colorless. The cooled mixture was extracted with ethyl acetate. The ethyl acetate extract and the toluene layer were mixed together. The acid obtained after removing the solvent mixture were esterified with diazomethane, prepared from 8 g. of nitrosomethyl urea, to furnish 4-methoxycarbonyl-6-(α-methoxycarbonylethyl)-9-methyldecalin (XVI), b.p. 145-50°/0.05 mm, yield 5.53 g. (70%). (Found: C, 68.99; H, 9.22. $C_{17}H_{28}O_4$ requires C, 68.92; H, 9.42%).

4-Hydroxymethyl-6-(α-hydroxymethylethyl)-9-methyldecalin (III).—Lithium aluminium hydride (1.7 g.) was refluxed with anhydrous ether (100 c.c.) for 20 mins. The ester (XVI) (7.5 g.) in anhydrous ether (200 c.c.) was then slowly added through the separatory funnel at such a rate as to maintain the reaction mixture at reflux. A gelatinous precipitate appeared immediately. After keeping for 1 hour, the reaction mixture was refluxed for one hour more and left overnight. The product was then decomposed with H_2SO_4 (dil.). To remove any unreduced ester, the product was refluxed for 10 hours with potassium hydroxide (3 g.) in water (3 c.c.) and methanol (25 c.c.). After removing the methanol the product was diluted with water and extracted with ether. The ether was removed and the residue distilled, b.p. 150-52°/9.3 × 10^{-2} mm, yield 4.4 g. (90%), (based on recovered acid). (Found : C, 74.96 ; H, 11.4. $C_{15}H_{28}O_2$ requires C, 75.01 ; H, 11.67%). Acidification of the alkaline solution furnished 1.3 g. of the unchanged acid.

4-Acetoxymethyl-6-(α-acetoxymethylethyl)-9-methyldecalin (IV).—A mixture of 4-hydroxymethyl-6-(α-hydroxymethylethyl)-9-methyldecalin (III) (4.8 g.), acetic anhydride (7 c.c.), and pyridine (1 c.c.) was refluxed for 3 hours. The excess of acetic anhydride was removed under diminished pressure. The reaction mixture was then taken in benzene and washed with water. After removing the solvent the product was distilled, b.p. 145-50°/3.5×10^{-2} mm, yield 5.6 g. (85%). (Found : C, 70.28 ; H, 9.77. $C_{19}H_{32}O_4$ requires C, 70.37 ; H, 9.87%).

Selinene Isomers.—The aforementioned diacetate (IV) (4.4 g.) was dropped in a 25 mm pyrex column, externally heated to 500-575° by an electric furnace and packed to a depth of 10 mm with pyrex helices. The addition was conducted in an inert atmosphere by introducing a slow stream of nitrogen at the top of the column. The pyrolysate was collected in a test tube, cooled in a freezing mixture (ice and salt). The pyrolysis product was taken up in ether and washed with water to free it from acetic acid. After removing the ether, the product was distilled, b.p. 113-15°/3 mm, n_D^{22} 1.5379 ; λ_{max}^{EtOH} 224 mμ, log ε 4.2 ; yield 0.8 g. (29%). (Found : C, 88.17: H, 11.81. $C_{15}H_{24}$ requires C, 88.25 ; H, 11.77%).

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IMPROVED SYNTHESIS OF 3 : 4-BENZOPYRENE-5-C^{14}*

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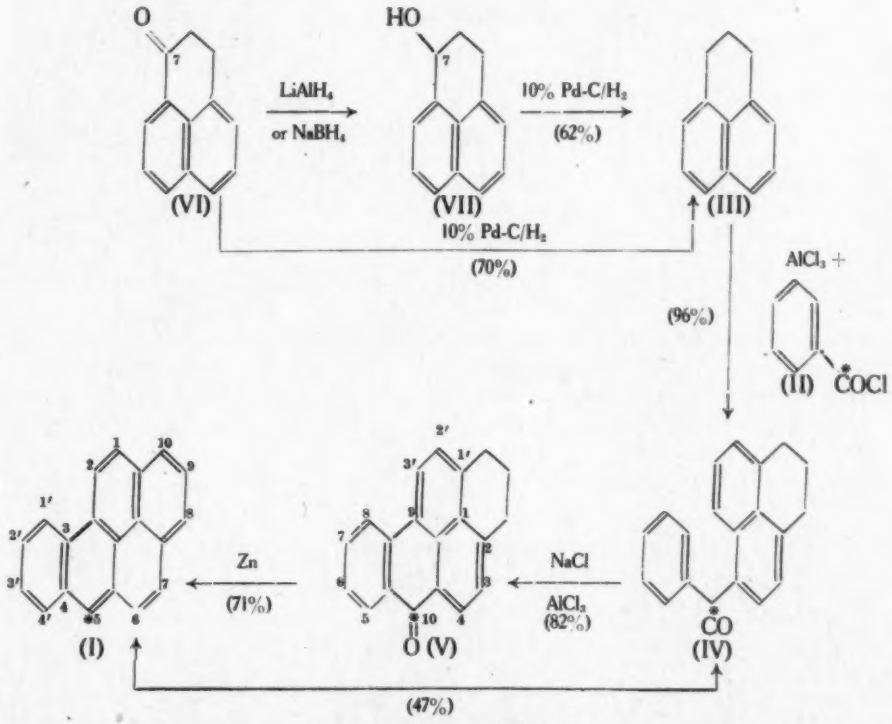
Synthesis of 3:4-benzopyrene-5-C^{14} has been achieved in a greater overall yield by modifications of the existing methods. Preparation of perinaphthane (III) of high purity in better yield from perinaphthanone-7 (VI) is also recorded.

In an extended study of the nature of the protein-bound acidic metabolite and its mode of formation on the skin after painting the test animals with the highly carcinogenic 3:4-benzopyrene (Tarbell *et al.*, *Cancer Res.*, 1956, **16,** 37), it became necessary to label the same hydrocarbon (I) at position 5 with C^{14}. Although the known synthetic route (Heidelberger and Reike, *ibid.*, 1951, **11,** 640; Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1938, **60,** 1658) (Chart I) was essentially followed, it is intended to record here some useful modifications developed, which improve the yield and simplify the procedure.

CHART I



Following the recorded methods (*loc. cit.*; Boekelheide and Larrabee, *J. Amer. Chem. Soc.*, 1950, **72,** 1240), we could not obtain the key material, perinaphthane (III), from perinaphthanone-7 (VI) in high yields with the high purity required for the radioactive synthesis. Attempted high pressure hydrogenation of perinaphthanol-7 (VII), the metal hydride reduction product of the

* The work reported here was entirely done in the Department of Chemistry, University of Rochester, Rochester, N.Y., U.S.A. during 1956-57.

ketone over copper chromite at 230° with varying amounts of catalyst (Boekelheide and Goldman, *J. Org. Chem.*, 1954, **19,** 575), did not result in more than 30-50% yield of the crude hydrocarbon. Finally, the hydrogenolysis of perinaphthanone-7 (VI) or the corresponding alcohol in methanol in presence of 10% Pd-C at ordinary temperature and pressure and purification through the picrate, m.p. 150-51°, provided perinaphthane of desired purity, m.p. 65-65.5°, in 70% yield.

With some manipulative modifications the synthesis of 2:1′-trimethylene-1:9-benzanthrone-10-C^{14}, m.p. 218.5-20°, in brilliant yellow leaflets proceeded smoothly.

Attempted conversion of the ketone to the hydrocarbon in stages was not very promising. Thereupon a variety of conditions was tried for the distillation of the ketone over activated zinc with a view to improving the yield. The best method has been recorded in the Experimental section. 3:4-Benzopyrene-5-C^{14} obtained in 37% overall yield, based on benzoic acid-carbonyl-C^{14}, is the highest yield reported so far.

EXPERIMENTAL*

Preparation of Perinaphthanol-7 (VII) *by the Sodium Borohydride Reduction of Perinaphthanone-7* (VI).—Perinaphthanone-7 (3 g.), obtained in about the same yield recorded in the literature by the chloromethylation of naphthalene by Coles and Dodds' method (*J. Amer. Chem. Soc.*, 1938, **60,** 853) and then following Fieser and Gates' (*ibid.*, 1940, **62,** 2335), was dissolved in ethanol (15 c.c.) to which sodium borohydride (1 g.) was added, and the mixture was left overnight. It was worked up in the usual way and on recrystallisation from benzene-petroleum ether, long stout colorless needles of perinaphthanol-7 in clusters (2.9 g.), m.p. 84-85°, were obtained. The mixed m.p. with a sample prepared by the $LiAlH_4$ reduction of the ketone (Boekelheide and Larrabee, *ibid.*, 1950, **72,** 1245) showed no depression. Quantitatively, the former method was found to be better.

Preparation of Perinaphthane (III): (*a*) *By the Hydrogenolysis of Perinaphthanol-7* (VII) *over* 10% Pd-C *Catalyst* (cf. Boekelheide and Goldman, *loc. cit.*).—Perinaphthanol-7 (10 g.) was dissolved in methanol (100 c.c.) and was shaken with hydrogen over 10% Pd-C catalyst, prepared according to Mozingo ("Organic Syntheses", 1946, Vol. 26, p.77), at ordinary temperature and pressure until no more absorption was observed. After removal of the catalyst and the solvent, the residue was taken up in ether and converted into the picrate, which on recrystallisation from methanol yielded orange-red needles (13.3 g.), m.p. 151-52°. The picrate on decomposition through alumina afforded pure, free hydrocarbon (5.7 g.), m.p. 65-65.5°, in 62% yield.

(*b*). *By Hydrogenolysis of Perinaphthanone-7* (VI) *over* Pd-C *Catalyst*.—Perinaphthanone-7 (10 g.) was dissolved in methanol (75 c.c.) and hydrogenated over 10% Pd-C at ordinary temperature and pressure. The hydrogenation was complete within 12 hrs. It was worked up as outlined before to yield 6.4 g. of perinaphthane (70%), m.p. 65-65.5°.

Attempted hydrogenolysis of the acetic acid solution (30 c.c.) of the ketone (2 g.) in a Parr apparatus over 5% Pd-C (1 g.) at an initial pressure of 37 lbs. and at 65° according to Horning and Reisner (*J. Amer. Chem. Soc.*, 1949, **71,** 1036) yielded a colorless oil (1.5 g.), b.p. 77°/0.5 mm. The oil did not form any picrate. The infrared spectrum of the liquid, however, showed the absence of the carbonyl peak. It might therefore be a ring-reduced product formed as a result of overhydrogenation. It was not investigated further.

* Melting points are uncorrected unless otherwise stated. Fisher adsorption alumina and petroleum ether (b.p. 30-60°) have been used throughout. The micro-analyses are in good agreement with the theory. The radioactive assays were done by the wet combustion followed by C^{14}- measurements by ionisation chamber technique using a Vibrating Reed Electrometer, Applied Physics Corporation (U.S.A.), Model No. 31.

Preparation of 3-*Benzoylperinaphthane-carbonyl*-C^{14} (IV).—Benzoyl chloride-carbonyl-C^{14} (1.261 g.) was prepared from benzoic acid-carbonyl-C^{14} (containing 12.53 mc. of radioactivity) according to Heidelberger and Reike (*loc. cit.*) in about the same yield, except that the benzene was removed at ordinary pressure at a bath temperature of 130-40°. It was diluted with unlabelled benzoyl chloride (0.7 g.); the carbond isulphide solution of the Perrier complex with aluminium chloride (1.92 g.) was added from a warm funnel to a solution of perinaphthane (2.27 g.) in the same solvent (the reverse addition decreased the yield to some extent) and worked up according to the recorded procedures (*loc. cit.*). The pale yellow, highly viscous 3-benzoylperinaphthane-carbonyl-C^{14} (3.085 g.) distilled at 218-20°/0.1 mm. From the sides and the cold finger of the still a further amount (0.574 g.) was recovered. The total yield was 96%.

Preparation of 2:1′-*Trimethylene*-1:9-*benzanthrone*-10.—It was prepared from benzoylperinaphthane (2.1 g.) in the same way as by Heidelberger and Reike (*loc. cit.*) excepting the modification mentioned below. After the reaction was over, the melt was poured into ice and HCl (1:1). Most of the melt, however, solidified in the reaction flask, which was scraped off, gradually decomposed, and left overnight. The product, collected at the bottom of the clear solution, was extracted with chloroform. The organic layer was washed, dried, and the solvent concentrated to a small volume. On addition of petroleum ether and keeping overnight, the dirty grey, granular mass (1.15 g.), easy to handle, was obtained. Further purification was effected by chromatography over alumina or by short-path distillation at 230-40°/0.1 mm. Crystallisations from benzene-acetone or precipitation with petroleum ether from chloroform solution yielded golden yellow flakes, m.p. 218.5-20° (corr.).

Attempted Reduction of the 2:1′-*Trimethylene*-1:9-*benzanthrone*-10 *with* $LiAlH_4$.—The ketone (0.39 g.) was treated with $LiAlH_4$ in tetrahydrofuran in the usual way. Crystallisation from benzene-methanol yielded orange leaflets, m.p. 216-218.5° (corr.). (Found : C, 88.42; H, 5.14. Calc. for $C_{20}H_{16}O$: C, 88.20; H, 5.92%; for $C_{20}H_{14}O$: C, 88.86; H, 5.22%).

Attempted Dehydrogenation of the $LiAlH_4$ *Reduction Product*: (*i*) *With* 10% Pd-C.—The crude product (0.2 g.) was thoroughly mixed with 10% Pd-C (0.4 g.) and heated under an atmosphere of dry nitrogen at 340-60° for 3 hrs. Some yellow glistening crystals collected at the cooler part. The benzene solution of the product was chromatographed through alumina and directly converted into picrate of benzopyrene (Cook *et al.*, *J. Chem. Soc.*, 1933, 396), m.p. 197-99°, but the yield was too poor (13 mg.) for this method to have any practical value.

(*ii*). *With* 30% Pd-C.—The substance (0.2 g.) was mixed with 30% Pd-C (Linstead and Thomas, *ibid.*, 1940, 1127) and heated at 35-55° for 3 hrs. The crude product was dissolved in benzene, to which petroleum ether was added. Long yellow needles embedded in the viscous oil separated. The m.p. of the crude product was above 220°. No further work was done with it.

Preparation of Benzopyrene-5-C^{14} (I).—2:1′-Trimethylene-1:9-benzanthrone-10-carbonyl-C^{14} (V), prepared in 82% yield from 3-benzoylperinaphthane-carbonyl-C^{14} (3.658 g.) by the precipitation method (*vide supra*), was distilled over activated zinc in three batches.

In a typical run, an intimate mixture of the ketone (1.039 g.) with 30 mesh activated zinc (Beerboom *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 3500; Fieser and Johnson, *ibid.*, 1940, **62**, 576) was introduced in the centre of a specially heat-resistant pyrex combustion tube (300 × 17 mm) and plugged with glass wool. A layer of activated zinc dust was made at both ends and plugged again. Dry nitrogen was passed through the tube, which was then introduced in a preheated (700°) furnace, while the stream of nitrogen continued. A tube from the other end was led through a

series of traps. The first two were cooled by dry ice-acetone and the last two contained benzene. All the connections were made as quickly as possible and the tube outside the furnace was cooled with wet cotton. Shortly after, heavy fumes were given off and dirty yellow distillate was collected at the cooler part. The operation was complete within 20 mins. The distillate was dissolved in ether; the residue was extracted with ether in a Soxhlet overnight and next with chloroform (to recover any unconverted starting material). The combined ether solution was concentrated and converted into the picrate. Recrystallisation from methanol yielded 1.316 g. (corresponding to 71% of benzopyrene based on the wt. of the ketone) of the crystallised material.

The total picrate from all the runs on two recrystallisations from the same solvent yielded 3.046 g. of dark purplish needles (corresponding to 1.596 g. of benzopyrene theoretically and 47% yield from 3-benzoylperinaphthane-carbonyl-C^{14}), m.p. 198-99° (Cook *et al.*, *loc. cit.*). The overall yield of the pure benzopyrene picrate, and hence that of benzopyrene based on benzoic acid-carbonyl-C^{14} is 37% containing the total radioactivity 6.134 mc. and specific activity 0.968 mc./m. moles respectively. We are unable to offer any satisfactory explanation for the observed higher activities.

A portion of the picrate (0.505 g.) was decomposed in the dark through a column (3×10 cm) of alumina using benzene as the solvent and eluent. The recovery of the hydrocarbon (0.227 g.) from the picrate was 86%. Recrystallisations from ethanol yielded yellow leaflets (0.15 g.) of benzopyrene, m.p. 176-77° (Cook *et al.*, *loc. cit.*), identified by the direct comparison with the purest sample available in our laboratory (Tarbell *et al.*, *loc. cit.*). For animal experiments, further chromatographic purification was done according to Heidelberger and Reike (*loc. cit.*).

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PHENOXIDES OF TUNGSTEN

BY SARJU PRASAD AND K. S. R. KRISHNAIAH

Tungsten phenoxides of some mono-, di-, and tri-hydroxyphenols and mono- and di-nitrophenols have been prepared by the action of tungsten(VI) chloride on these phenols, their properties studied, and their constitutions discussed.

Funk and Baumann (*Z. anorg. allgem. Chem.*, 1937, **231**, 264) studied the action of WCl_6 on phenol and β-naphthol. They obtained $WCl_2(PhO)$ by digesting WCl_6 with PhOH in the presence of CCl_4 on a water bath and $W(PhO)_6$ by the action of WCl_6 on PhOH. In a similar manner they obtained $WCl_2(C_{10}H_7O)_4$ and $W(C_{10}H_7O)_6$. Fernandes (*Gazzetta*, 1925, **55**, 424, 40) prepared the complexes of pyrocatechol and pyrogallol with MoO_2, WO_3, and UO_2.

The present communication deals with a study of the phenoxides of tungsten by the action of some mono-, di-, and tri-hydroxyphenols and mono- and di-nitrophenols on tungsten(VI) chloride.

EXPERIMENTAL

The phenols and nitrophenols used were of B.D.H. or Merck's 'extra' pure quality. Ether (AnalaR) was distilled over metallic sodium.

Tungsten(VI) chloride was prepared by the action of chlorine on pure tungsten powder (Messrs. Johnson and Matthey) at 600° in a quartz tube in the complete absence of oxygen. Traces of tungsten(VI) oxychlorides were also formed but were sublimed off. Excess of chlorine was removed by passing well-dried, oxygen-free nitrogen. A solution of tungsten(VI) chloride, dissolved in anhydrous ether, was used in all the experiments.

General Method.—Ethereal solutions of WCl_6 and phenol or nitrophenol were mixed together; the mixture was slowly warmed at about 50-60° in an oil bath for about half an hour. The temperature of the bath was then slowly raised and finally the residue was heated at a temperature of 10-12° higher than the m.p. of the respective phenol. The heating was continued till the evolution of HCl had ceased. In all the cases the reaction was carried out in an atmosphere of nitrogen. The compounds obtained were washed with anhydrous ether and dried in vacuum. As the products obtained with resorcinol and orcinol were hygroscopic, these were quickly transferred to a vacuum desiccator and dried for 2-3 days.

A weighed quantity of the compound was digested with HNO_3 (conc.) for several hours on a water bath. It was then evaporated to dryness, ignited, and weighed as WO_3.

Carbon and hydrogen were estimated in a few cases by combustion method and in the rest, the organic matter in the compound was found by difference. Nitrogen was estimated by Duma's method.

General Properties.—All the compounds are coloured, insoluble in CCl_4, ether, and benzene but sparingly soluble in ethanol and acetone. The compounds formed with *o*-, *m*-, and *p*-cresols are, however, sparingly soluble in CCl_4, ether, and benzene and soluble in ethanol and acetone. These are very stable in dry atmosphere, hydrolyse slowly on boiling with water, decompose when treated with acids or alkalies, and do not exhibit any coloration with ferric chloride.

TABLE I

Phenols.	Compound formed.	Colour.	% Tungsten. Found.	Calc.	% Org. matter. Found.	Calc.
A. Tungsten(VI) chloride with monohydroxyphenols. WCl_6 : phenol = 1 : 6.						
α-Naphthol	$(C_{10}H_7O)_6W$	Black	17.37	17.65	82.63	82.35
					C: 69.46	69.10
					H: 4.25	4.03
o- Cresol	$(CH_3.C_6H_4O)_6W$	Greyish black	22.59	22.27	77.41	77.73
m- ,,		Black	22.24		77.76	
p- ,,		,,	22.40		77.60	
o- Nitrophenol	$(NO_2.C_6H_4O)_6W$	,,	18.12	18.18	81.88	81.82
					C: 42.46	42.70
					H: 2.20	2.37
					N: 8.28	8.30
m- ,,		,,	18.26		81.74	81.82
					N: 8.29	8.30
p- ,,		,,	18.34		81.66	81.82
					N: 8.16	8.30
2 : 4-Dinitrophenol	$[(NO_2)_2.C_6H_3O]_6W$	Greyish brown	14.68	14.34	85.32	85.66
					N: 12.96	13.10
2:4-Dinitro-α-naphthol	$[(NO_2)_2.C_{10}H_3O]_6W$	Shining black	11.86	11.63	88.14	88.37
					N: 10.74	10.62
B. Tungsten(VI) chloride with dihydroxyphenols. WCl_6 : phenol = 1 : 3.						
Pyrocatechol	$(C_6H_4O_2)_3W$	Black	36.10	36.22	63.90	63.78
					C: 42.68	42.53
					H: 2.24	2.36
Resorcinol		Deep reddish brown	36.24	36.22	63.76	63.78
Hydroquinone		Black	36.59	36.22	63.41	63.78
Orcinol	$(CH_3.C_6H_3O_2)_3W$	,,	33.68	33.45	66.32	66.55
C. Tungsten(VI) chloride with trihydroxyphenols. WCl_6 : phenol = 1 :2.						
Pyrogallol	$(C_6H_3O_3)_2W$	Pitch-black	42.90	42.79	57.10	57.21
					C: 33.68	33.49
					H: 1.46	1.40
Phloroglucinol		Chocolate-brown	42.56	42.79	57.44	57.21

DISCUSSION

From the results it is evident that one molecule of tungsten(VI) chloride reacts with six molecules of a monohydroxy and three molecules of a dihydroxy and two molecules of a trihydroxy phenol. Nitro- and dinitro-phenols give similar results, only the hydroxy group being affected. The compounds formed can be represented as $W(C_{10}H_7O)_6$, $W(C_6H_4O_2)_3$, and $W(C_6H_3O_3)_2$ in the case of mono-, di-, and trihydroxy phenols respectively.

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BEHAVIOUR OF ELECTROLYTES IN MIXED SOLVENTS. PART VI. VISCOSITY OF MAGNESIUM CHLORIDE AND POTASSIUM SULPHATE IN DIOXANE-WATER MIXTURES AT 35°

BY P. B. DAS, P. K. DAS AND D. PATNAIK

The viscosities of magnesium chloride and potassium sulphate in dioxane-water mixtures at 10, 20, and 30% by weight of dioxane have been studied at 35°. The data fit well with the modified form of the Jones-Dole equation. The value of B has been found dependent on the solvent composition in case of both the electrolytes.

The modified Jones-Dole equation,

$$\frac{\eta_l}{\eta_0} = 1 + A\sqrt{C} + BC^x,$$

suggested by us (*Curr. Sci.*, 1956, **25**, 337) has been found to apply in case of mono-monovalent electrolytes like KCl and NaCl in dioxane-water mixtures at 35° (this *Journal*, 1957, **34**, 56; 1959, **36**, 613). With a view to verifying the applicability of the equation in case of bi-monovalent and uni-bivalent type of electrolytes, the viscosities of $MgCl_2$ and K_2SO_4 in 10, 20, and 30% dioxane-water mixtures by weight have been determined at 35°.

EXPERIMENTAL

$MgCl_2$ and K_2SO_4 used were of B.D.H. AnalaR quality. The estimation of Mg^{2+} and Cl^- content and the recrystallisation of K_2SO_4 have been described previously (*loc. cit.*). The preparation of the solvents, solutions and measurements of viscosity and conductance were the same as reported earlier (*loc. cit.*).

TABLE I

Solvent composition.	$MgCl_2$			K_2SO_4		
	$A\times10^2$.	B.	x.	$A\times10^2$.	B.	x.
10	1.640	0.43	1.00	1.300	0.28	1.00
20	1.830	0.54	0.95	1.500	0.30	0.99
30	2.055	0.84	1.05	2.600	0.38	0.94

TABLE II

Salts.	Conc. (moles/litre)	Observed viscosity.	Calc. viscosity by J. D.	Calc. viscosity by Modified J.D.
$MgCl_2$	0.100	1.0662	1.0598	1.0664
	0.001	1.0014	1.0011	1.0014
K_2SO_4	0.100	1.0354	1.0347	1.0353
	0.001	1.0008	1.0008	1.0008

DISCUSSION

The change in viscosity with concentration for aqueous solution of electrolytes is satisfactorily represented by the Jones-Dole equation (*loc. cit.*). The evaluation of the equivalent conductance (Λ_o) at zero concentration and the calculation of '*A*' by the Falkenhagen and Vernon expression have been reported earlier (*loc. cit.*). The usual procedure to test the Jones-Dole equation has been applied, and it has been found that the equation holds good only for 10% dioxane solvent composition. For 20% and 30% solvent composition, the Jones-Dole equation is, however, inadequate, and its modified form represents the experimental results satisfactorily.

The values of *A*, *B* and, *x* for different solvent compositions can be calculated as described previously. These values for solutions of $MgCl_2$ and K_2SO_4 at different solvent compositions are recorded in Table I. The relative viscosities were next calculated by the use of these determined values of *B* and *x*. Calculated and observed values are in good agreement for the range of concentrations of the solute 0.100*M* to 0.001*M* investigated at 10, 20, and 30% dioxane composition. Only two data for each of the electrolytes at 20% solvent composition have been recorded in Table II for illustration.

The data recorded in Table I show that with increase of the dioxane content in the solvent the value of *B* also increases, indicating its dependence on the composition of the solvent.

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ORGANIC PESTICIDES. PART III. SYNTHESIS OF AMIDE DERIVATIVES OF FLUOROPHENOXYCARBOXYLIC ACIDS

By K. C. Joshi and S. C. Bahel

A large number of amide derivatives of fluorophenoxycarboxylic acids have been synthesised as possible biologically active compounds and plant-growth regulators.

Although the role of halogenated amides as pest control chemicals has been studied extensively, very little information is available on the fluoro or mixed fluoro-halogen analogues. Recently Mitchell *et al.* (*J. Agric. Food Chem.*, 1959, **7**, 118) have reported the synthesis of amide, lactic acid, and terpenoid derivatives of chlorinated phenoxycarboxylic acids, possessing interesting biological activity including growth-regulating properties. This activity has been attributed both to the presence of an amide group on the side chain of chlorinated phenoxy acids and the position and degree of chlorination on the benzene nucleus. It has been observed that the amides of chlorinated phenoxyacetic acids are more effective in retarding mature fruit abscission than the corresponding acids.

Keeping these observations in view, we have synthesised a large number of amide derivatives of fluorophenoxycarboxylic acids as potential biologically active compounds. The fluorophenoxy acids have already been prepared by us (Joshi and Bahel, this *Journal*, 1960, **37**, 365). The *p*-aminobenzoic acid and *p*-aminosalicylic acid derivatives have been obtained by following the method of Mitchell *et al.* (*loc. cit.*).

The pesticidal and other biological activities of these compounds will be communicated in due course.

Experimental

Fluorophenoxy Acid Chlorides.—*o*-Fluorophenoxyacetic, *p*-fluorophenoxyacetic and *p*-fluorophenoxypropionic acids were prepared by the method reported earlier (*loc. cit.*). A mixture of the appropriate fluorophenoxy acid (20 g.) and thionyl chloride (50 g.) was refluxed gently for about 3 hours on a steam bath; the excess of thionyl chloride was removed and the acid chlorides were distilled as colorless liquids. The following acid chlorides were obtained.

TABLE I

	Acid chloride.	B.P.	Yield.	Formula.	% Carbon.		% Hydrogen.	
					Found.	Calc.	Found.	Calc.
1.	*o*-Fluorophenoxyacetyl	150-55°/70-75 mm	83.4%	$C_8H_6O_2ClF$	51.54	50.95	3.73	3.20
2.	*p*-Fluorophenoxyacetyl	* 140-45°/70-80	83.2	$C_8H_6O_2ClF$	51.33	50.95	3.68	3.20
3.	*p*-Fluorophenoxypropionyl	170°/150	84.1	$C_9H_8O_2ClF$	52.85	53.35	3.76	3.90

* Lit. 106-107°/9 mm.

Amide Derivatives of Fluorophenoxycarboxylic Acids.—A solution of the appropriate amine (2 *M*) in dry benzene was added dropwise with frequent shaking to a solution of the acid chloride (1 *M*) in dry benzene. The reaction mixture was refluxed for 1 to 2 hours over a steam bath, left overnight, and then filtered. The precipitate was washed with a small quantity of warm benzene, which was subsequently mixed with the original benzene extract. The combined extract was washed with 2% sodium carbonate solution, followed by 2% HCl, and finally with water. After removal of the benzene the residual amide was recrystallised from aqueous ethanol. The

amides obtained are listed below. To confirm further their amide nature, some of the compounds were hydrolysed and the acids obtained were characterised by their melting points and neutralisation equivalents. In all cases, the parent acids were obtained.

TABLE II

	Amide.	M.P. or B.P.	Yield.	Formula.	% Nitrogen. Found.	Calc.
(1)	p-F*	108°	40%	$C_8H_6O_2NF$	8.25	8.28
(2)	*N*-Ethyl *p*-F	73°	84	$C_{10}H_{12}O_2NF$	6.81	7.10
(3)	*N*-(Butyl^n) *p*-F	39°	42	$C_{12}H_{16}O_2NF$	5.78	6.16
(4)	*N*-Benzyl *p*-F	98°	70	$C_{15}H_{14}O_2NF$	5.10	5.40
(5)	*N*-Phenyl *p*-F	96°	56	$C_{14}H_{12}O_2NF$	5.66	5.71
(6)	*N*-(*o*-Chlorophenyl) *p*-F	103°	65	$C_{14}H_{11}O_2NClF$	4.84	5.00
(7)	*N*-(*p*-Chlorophenyl) *p*-F	144°	67	$C_{14}H_{11}O_2NClF$	4.83	5.00
(8)	*N*-(*o*-Phenetyl) *p*-F	64°	50	$C_{16}H_{16}O_2NF$	4.91	4.84
(9)	*N*-*cyclo*Hexyl *p*-F	210-205°/80-90 mm	48	$C_{13}H_{16}O_2NF$	4.51	5.62
(10)	*N*-(*N*-Ethylphenyl) *p*-F	210-205°/100-20 mm	50	$C_{16}H_{17}O_2NF$	4.91	5.12
(11)	*o*-F	120°	45	$C_8H_6O_2NF$	8.29	8.28
(12)	*N*-Ethyl *o*-F	59°	85	$C_{10}H_{12}O_2NF$	6.74	7.10
(13)	*N*-Benzyl *o*-F	69°	90	$C_{15}H_{14}O_2NF$	5.64	5.40
(14)	*N*-Phenyl *o*-F	105°	83	$C_{14}H_{12}O_2NF$	5.68	5.71
(15)	*N*-(*o*-Bromophenyl) *o*-F	99°	65	$C_{14}H_{11}O_2NBrF$	4.20	4.32
(16)	*N*-(*m*-Bromophenyl) *o*-F	97°	70	$C_{14}H_{11}O_2NBrF$	4.15	4.32
(17)	*N*-(*o*-Anisyl) *o*-F	65°	60	$C_{15}H_{14}O_3NF$	4.91	5.09
(18)	*N*-(*o*-Tolyl) *o*-F	107°	88	$C_{15}H_{14}O_2NF$	5.70	5.40
(19)	*N*-(*m*-Tolyl) *o*-F	84°	86	$C_{15}H_{14}O_2NF$	5.68	5.40
(20)	*p*-F'*	83°	50	$C_9H_{10}O_2NF$	7.45	7.65
(21)	*N*-Ethyl *p*-F'	48°	92	$C_{11}H_{14}O_2NF$	6.59	6.63
(22)	*N*-Benzyl *p*-F'	62°	88	$C_{16}H_{16}O_2NF$	5.09	5.12
(23)	*N*-Phenyl *p*-F'	106°	75	$C_{15}H_{14}O_2NF$	5.20	5.40
(24)	*NN*-Diethyl *p*-F'	26°	45	$C_{13}H_{18}O_2NF$	6.20	6.51

* F denotes fluorophenoxyacetamide and F', α-(fluorophenoxy)-propionamide.

N-(p-*Fluorophenoxyacetyl*)-p-*aminosalicylic acid* was prepared by the method of Mitchell *et al.* (*loc. cit.*) by condensing *p*-aminosalicylic acid (2 g.) with *p*-fluorophenoxyacetyl chloride (3 g.), m.p. 130°, yield 1.7 g. (35% of theory). (Found: N, 4.34. Calc. for $C_{15}H_{12}O_5NF$: N, 4.59%).

N-(p-*Fluorophenoxypropionyl*)-p-*aminobenzoic acid* was prepared by the above method from *p*-aminobenzoic acid (3.5 g.) and *p*-fluorophenoxypropionyl chloride (5 g.), m.p. 78-79°, yield 4 g. (53% of theory). (Found: N, 4.48. Calc. for $C_{16}H_{14}O_4NF$: N, 4.62%).

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ORGANIC PESTICIDES. PART IV. SYNTHESIS OF CERTAIN FLUORO-HYDROXYKETONES AND THEIR ALLYL ETHERS

By K. C. Joshi and S. C. Bahel

For studying pesticidal activity, a dozen fluorohydroxyketones have been synthesised by the Fries rearrangement of esters of *p*-fluorophenol, and six of them have been converted into their allyl ethers.

Hydroxyketones and their allyl ethers are well known as contact insecticides in view of their having a combination of toxic and lipoid-soluble groupings in the molecule (Lauger *et al.*, *Helv. Chim. Acta*, 1944, **27**, 918). Recently Buu-Hoï *et al.* (*J. Org. Chem.*, 1953, **18**, 910; 1954, **19**, 1617) have reported the synthesis of certain fluorohydroxyketones exhibiting biologically interesting properties.

Keeping these observations in view, we have now prepared fluorohydroxyketones and fluoroallyl ethers as potential pesticides. Twelve esters of *p*-fluorophenol were obtained by the action of the appropriate acid chloride on the phenol. These esters were subjected to the Fries rearrangement at 130° without a solvent. In all cases, *o*-hydroxyketones were obtained responding to Pyman's test (*J. Chem. Soc.*, 1930, 280). Six of these hydroxyketones were converted into their allyl ethers.

Experimental

Esters

p-Fluorophenol was prepared by following the method of English *et al.* (*J. Amer. Chem. Soc.*, 1940, **62**, 350).

Twelve new esters of *p*-fluorophenol were prepared by heating for 2 hours a reaction mixture of the appropriate acid chloride (0.1 *M*), *p*-fluorophenol (0.1 *M*), anhydrous benzene (25 c.c.), and Mg ribbon (1.2 g.). After cooling, the benzene was distilled off and the residue taken into ether. The ethereal layer was washed with 1% NaOH solution and water, dried, the ether removed, and the residual product either distilled under reduced pressure or alternatively recrystallised from aqueous ethanol. The following esters have been obtained.

TABLE I

Esters of p-*fluorophenol.*

Sl. No.	1-Hydroxy-4-fluorophenyl esters.	%Yield.	B.P. or M.P.	Formula.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
1.	Monochloroacetate	57.8	177°/10mm	$C_8H_6O_2ClF$	51.16	50.92	3.32	3.18
2.	α-Chloropropionate	62.8	185°/15	$C_9H_8O_2ClF$	53.32	53.59	4.20	3.97
3.	α-Crotonate	70.0	155-60°/5	$C_{10}H_9O_2F$	66.38	66.66	4.80	5.00
4.	Caproate[n]	67.3	140°/2	$C_{12}H_{15}O_2F$	68.19	68.57	6.97	7.14
5.	*o*-Chlorobenzoate	88.0	182°/30	$C_{13}H_8O_2ClF$	62.52	62.27	3.32	3.15
6.	*p*-Fluorobenzoate	88.4	77°	$C_{13}H_8O_2F_2$	66.46	66.66	3.24	3.41
7.	*m*-Methylbenzoate	97.3	185-90°/17	$C_{14}H_{11}O_2F$	73.28	73.04	4.63	4.78
8.	*p*-Methoxybenzoate	79.4	57°	$C_{14}H_{11}O_3F$	68.44	68.29	4.23	4.47
9.	Caprylate[n]	85.9	165°/17	$C_{14}H_{19}O_2F$	70.29	70.58	8.19	7.98
10.	Cinnamate	95.8	67°	$C_{15}H_{11}O_2F$	74.08	74.38	4.32	4.54
11.	Caprate[n]	78.2	167°/12	$C_{16}H_{23}O_2F$	73.36	72.18	8.46	8.64
12.	Laurate	86.7	205°/20	$C_{18}H_{27}O_2F$	73.19	73.46	9.32	9.18

Fries Rearrangement of the Esters.—The rearrangement was carried out by heating the ester (0.06*M*) and anhydrous aluminium chloride (0.1*M*) for 2 hours at 130° (Sen and Tewari, this *Journal*, 1952, **29**, 421). The *o*-hydroxyketones were isolated and purified in the usual manner, and characterised through their 2 : 4-dinitrophenylhydrazones. Analytical data, m.p., b.p., and yields of the compounds synthesised are recorded in Table II.

TABLE II

	Fluorohydroxy ketones *.						2:4-Dinitrophenylhydrazones.			
† Ketones.	% Yield.	B.P. or M.P.	%Carbon. Found.	%Carbon. Calc.	%Hydrogen. Found.	%Hydrogen. Calc.	M.P.	Formula.	%Nitrogen. Found.	%Nitrogen. Calc.
1. R-chloromethyl-K	50.0	177°/10mm	51.13	50.92	3.32	3.18	160°	$C_{13}H_{10}O_5N_4ClF$	14.83	15.11
2. R-α-chloroethyl-K	50.0	185°/5	53.36	53.59	3.80	3.97	170°	$C_{15}H_{12}O_5N_4ClF$	14.21	14.60
3. R-propenyl-K	20.0	71°	66.35	66.66	5.18	5.00	150°	$C_{16}H_{13}O_5N_4F$	15.32	15.47
4. R-amyl^n-K	87.5	31°	68.23	68.57	7.32	7.14	176°	$C_{18}H_{19}O_5N_4F$	14.40	14.36
5. R-*o*-chlorophenyl-K	95.8	65°	62.40	62.27	2.97	3.15	178°	$C_{19}H_{12}O_5N_4ClF$	12.44	12.94
6. R-*p*-fluorophenyl-K	83.3	205°/30	66.95	66.66	3.18	3.41	210°	$C_{19}H_{12}O_5N_4F_2$	13.15	13.46
7. R-*m*-tolyl-K	92.8	185°/15	72.83	73.04	4.59	4.78	233°	$C_{20}H_{15}O_5N_4F$	13.14	13.59
8. R-*p*-methoxyphenyl-K	60.0	260°/30	68.50	68.29	4.29	4.47	211°	$C_{20}H_{15}O_6N_4F$	12.77	13.08
9. R-heptyl^n-K	95.0	47°	70.36	70.58	8.21	7.98	141°	$C_{25}H_{29}O_5N_4F$	12.74	13.31
10. R-styryl-K	52.4	185-90°/20-25	74.58	74.38	4.29	4.54	175°	$C_{22}H_{15}O_5N_4F$	13.12	13.20
11. R-nonyl^n-K	55.5	270°/5	72.46	72.18	8.56	8.64	98°	$C_{27}H_{37}O_5N_4F$	12.29	12.50
12. R-undecyl^n-K	50.0	320°/10	73.19	73.46	9.35	9.18	105°	$C_{30}H_{43}O_5N_4F$	11.50	11.76

N.B. The esters correspond to those listed in Table I.

* The M.W.s of the ketones are the same as that of the respective esters from which they have been prepared by the Fries migration.

† R=5-fluoro-2-hydroxyphenyl; K=ketone.

Allyl-aryl Ethers

A mixture of allyl bromide (0.11 *M*), freshly fused potassium carbonate (0.15 *M*), *o*-hydroxyketone (0.1 *M*), and dry acetone (100 c.c.) was refluxed on a steam bath for 8-10 hours. After cooling and adding water, the oily layer separating was taken in ether, purified by repeated washings with 10% NaOH solution and water, dried, the ether removed, and the residual liquid distilled under reduced pressure. The allyl ethers obtained are listed in Table III.

TABLE III

Allyl ethers.

	o-Hydroxyketones.	*Ethers.	%Yield.	B.P.	Formula.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
1.	R-propenyl-K	R'-propenyl-K	98.1	190°/10mm	$C_{13}H_{13}O_3F$	70.63	70.90	6.18	5.90
2.	R-amyl^n-K	R'-amyl^n-K	84.0	185°/25	$C_{18}H_{19}O_3F$	72.28	72.00	7.38	7.60
3.	R-*o*-chlorophenyl-K	R'-*o*-chlorophenyl-K	86.2	215°/25	$C_{16}H_{12}O_3ClF$	65.86	66.09	3.88	4.13
4.	R-*p*-fluorophenyl-K	R'-*p*-fluorophenyl-K	99.1	170°/40	$C_{16}H_{12}O_3F_2$	81.78	82.05	4.98	5.12
5.	R-heptyl^n-K	R'-heptyl^n-K	68.6	190°/15	$C_{17}H_{23}O_3F$	73.09	73.38	8.03	8.27
6.	R-styryl-K	R'-styryl-K	68.5	220°/12	$C_{18}H_{15}O_3F$	76.29	76.56	5.16	5.31

N.B. K=ketone.
R=5-fluoro-2-hydroxyphenyl.
R'=1-allyloxy-4-flurophenyl.

The pesticidal activity of these compounds is under investigation and will be communicated in due course.

Thanks of the authors are due to the Council of Scientific and Industrial Research, New Delhi, for the award of a junior research fellowship to one of them (S.C.B.) and to Dr. R. C. Mehrotra, Professor and Head of the Department of Chemistry, University of Gorakhpur, for providing all departmental facilities.

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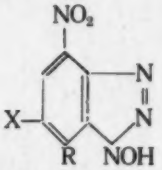
BEHAVIOUR OF CHLORONITROBENZENES WITH HYDRAZINE AND HYDRAZINE DERIVATIVES. PART XI. SUBSTITUTED 1-HYDROXY-1 : 2 : 3-BENZOTRIAZOLES AND THEIR DERIVATIVES

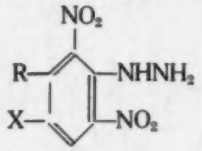
By Shiam Sunder Joshi and Daleep Singh Deorha

A few 1-hydroxy-1:2:3-benzotriazoles have been obtained by condensation of halogenopolynitrobenzenes with hydrazine hydrate or base-catalysed cyclisation of substituted nitrophenylhydrazines. Where formation of more than one product is possible, only one triazole derivative can be isolated. Structures to these compounds have also been assigned.

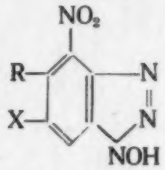
It has been shown in Part III of the series (Joshi and Deorha, this *Journal*, 1952, **29**, 545) that triazole formation can take place in two ways with nitrophenylhydrazines having both NO_2 groups in *ortho* position to the hydrazino group, the benzene ring being unsymmetrically substituted. Actually only one compound was isolated from the reaction product. Our previous findings (*loc. cit.*) have been confirmed in case of 4-bromo-2 : 6-dinitro-3-methyl-(Ia), 4-chloro-2 : 6-dinitro-3-methyl-(Ib) and 2 : 4 : 6-trinitro-3-methyl-(Ic) phenylhydrazines. From each of them two isomeric hydroxybenzotriazoles, *i.e.*, (IIa) and (IIIa) from (Ia), (IIb) and (IIIb) from (Ib), and (IIc) and (IIIc) from (Ic) could be expected, but only one from each has been isolated.



(III : a, b, c.)



(I)



(II : a, b, c.)

a : $R=CH_3$, $X=Br$
b : $R=CH_3$, $X=Cl$
c : $R=CH_3$, $X=NO_2$

To assign definite structure to each of the hydroxybenzotriazoles formed, the nitro group present in the molecule is replaced by a halogen atom and the identity of the dihalogenotriazole so formed is established. Thus, the triazole from (Ia) on reduction of the nitro group and subsequent replacement of the amino group by a bromine atom furnishes a dibromomethylhydroxybenzotriazole ; the methyl group in this compound can be either in 5 or 7 position. It is, however, identical with the product obtained by replacing the nitro group with a bromine atom in 4-bromo-6-nitro-7-methyl-1-hydroxy-1 : 2 : 3-benzotriazole. As in the latter compound (which is formed by cyclisation of 6-bromo-2 : 4-dinitro-3-methylphenylhydrazine) the methyl group is in position 7, the product of cyclisation of (Ia) should also have the methyl group in that position (*i.e.*, 7) and therefore must be (IIIa).

Following a similar procedure, the triazoles from (Ib) and (Ic) have been assigned structures (IIIb) and (IIIc) respectively (Table IV).

It appears from the above that in all cases, where the reaction can take two alternative courses, the nitro group adjacent to the methyl group is involved in the cyclisation.

Solutions of hydroxytriazoles in ethanol or of their sodium or ammonium salts in water form precipitates with soluble salts of silver, lead, mercury, and barium. Those obtained from hydroxytriazoles having no nitro group are colorless ; others vary in colour from yellow to dark red.

The silver salts of hydroxybenzotriazoles are very useful. These are obtained in pure condition easily; when decomposed with dilute hydrochloric acid these form silver halide in quantitative yields. The silver halide can be freed of the triazole by washing with ethanol. During the present work this reaction has been utilised for determining the molecular weights of the different hydroxybenzotriazoles. 6-Chloro-4-nitro- and 6-bromo-4-nitro-1-hydroxy-1 : 2 : 3-benzotriazoles afford deep red precipitates with minute quantities of soluble silver salts. These can therefore be employed for the detection of silver, even in traces, in presence of other metals, and have been successfully tried as spot test reagents for silver. Further work on the use of these reagents in inorganic analyses is in progress.

EXPERIMENTAL

The triazoles, described in Tables I and II, were prepared by Methods I and II reported earlier (Joshi and Deorha, *loc. cit.*).

TABLE I

S. No.	Halogenonitrobenzene used.	1-Hydroxy-1:2:3-benzotriazole formed.	Phenylhydrazine used.
1.	1:2-Dibromo-4:6-dinitro-5-methyl-	4-Bromo-6-nitro-7-methyl-	2-Bromo-4:6-dinitro-5-methyl-
2.	2-Chloro-1-bromo-4:6-dinitro-5-methyl-	4-Chloro-6-nitro-7-methyl-	2-Chloro-4:6-dinitro-5-methyl-
3.	1:4-Dibromo-2:6-dinitro-3-methyl-	6-Bromo-4-nitro-5-(or 7-)methyl-	4-Bromo-2:6-dinitro-3-methyl-
4.	4-Chloro-1-bromo-2:6-dinitro-3-methyl-	6-Chloro-4-nitro-5-(or 7-) methyl-	4-Chloro-2:6-dinitro-3-methyl-
5.	1-Chloro-2:4:6-trinitro-3-methyl-	4:6-Dinitro-5-(or 7-) methyl-	2:4:6-Trinitro-3-methyl-

TABLE II

*Triazole.	% Yield by Method I.	% Yield by Method II.	M.P.	Colour.	Formula.	Found.	Calc.
1.	65	18	225°	Light yellow	$C_7H_3O_3N_4Br$	Br: 29.41% **M: 272.50	29.30% 273.00
2.	60	14	218°	Pink	$C_7H_3O_3N_4Cl$	Cl: 15.31 M: 227.90	15.53 228.50
3.	79	70	204°	Cream	$C_7H_3O_3N_4Br$	Br: 29.18 M: 272.30	29.30 273.00
4.	76	68	195°	Golden yellow	$C_7H_3O_3N_4Cl$	Cl: 15.62 M: 227.10	15.53 228.50
5.	48	20	191°	Golden orange	$C_7H_3O_9N_5$	N: 29.41 M: 238.87	29.28 239.00

* Number corresponds to those recorded in Table I.

** M denotes mol. wt.

TABLE III

Acetyl derivatives.

*Triazole.	Colour.	M.P.	Formula.	Found.	Calc.
1.	Colorless	155°	$C_9H_7O_4N_4Br$	Br:24.91%	25.39%
2.	,,	132°	$C_9H_7O_4N_4Cl$	Cl:12.80	13.12
3.	,,	145°	$C_9H_7O_4N_4Br$	Br:25.14	25.39
4.	,,	140°	$C_9H_7O_4N_4Cl$	Cl:12.9	13.12
5.	Light yellow	175°	$C_9H_7O_6N_5$	N: 25.18	24.91

* The number of the triazole derivatives corresponds to those listed in Table I.

Conversion of a Halogenonitromethylhydroxybenzotriazole to a Dihalogenomethylhydroxybenzotriazole

Reduction.—A solution of the nitrohydroxytriazole (0.4 *M*) in ethanol, HCl (conc.), and iron in requisite amounts were refluxed for 2½ hours. After filtration the solution was made alkaline with NaOH and the alcohol removed. The precipitated iron hydroxide was separated, the filtrate was acidified with HCl, and evaporated to dryness. The amino compound formed was not isolated ; the residue was used as such in the subsequent preparations.

Diazotisation and Replacement of the Diazo Group by Halogen Atom.—The residue was dissolved in water (10 c.c.) and HCl (conc., 15 c.c.) was added. The mass was cooled in an ice bath and diazotised with aqueous sodium nitrite (4 g.). Reduced copper (0.2 g.) was added to the filtrate and the mixture was left overnight. Again the product was filtered and the filtrate evaporated to dryness. The residue on crystallisation from water furnished dihalogenomethyl-1-hydroxy-1 : 2 : 3-benzotriazole.

To substitute the amino group by a bromine atom, hydrobromic acid instead of hydrochloric acid was employed. When two amino groups were to be replaced by two chlorine atoms, double the quantities of hydrochloric acid and sodium nitrite (required for diazotisation) were used.

The products 1, 3 and 4 mentioned in the following table were found to be identical; so were 2 and 5. As in the dihalogenated triazoles No. 4 and 5 the methyl group is in position 7, it is confirmed that in the triazoles No. 1, 2 and 3 also, methyl group occupies the same position.

TABLE IV

No.	Triazole.	Dihalogenated triazole formed.	M.P.	Colour.	Formula.	Found.	Calc.	Position of Me.
1.	6-Chloro-4-nitro-5-(or 7-) methyl-	4:6-Dichloro-5(or 7)-methyl-	206°	Colorless	$C_7H_5ON_3Cl_2$	Cl: 32.42	32.56	7
2.	6-Bromo-4-nitro-5-(or 7-) methyl-	4:6-Dibromo-5(or 7)-methyl-	210°	,,	$C_7H_5ON_3Br_2$	Br: 52.23	52.11	7
3.	4:6-Dinitro-5-(or 7-) methyl-	4:6-Dichloro-5 (or 7)-methyl-	205°	,,	$C_7H_5ON_3Cl_2$	Cl: 32.68	32.56	7
4.	4-Chloro-6-nitro-7-methyl-	4:6-Dichloro-7-methyl-	206°	,,	$C_7H_5ON_3Cl_2$	Cl: 32.38	32.56	
5.	4-Bromo-6-nitro-7-methyl-	4:6-Dibromo-7-methyl-	210°	,,	$C_7H_5ON_3Br_2$	Br: 52.39	52.11	

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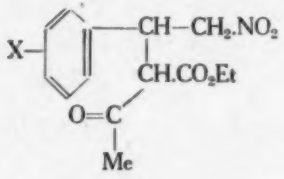
SYNTHESIS OF SUBSTITUTED INDENES

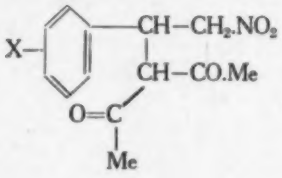
By K. L. Pathak and B. Pathak

β-Nitrostyrenes have been condensed with acetoacetic ester as well as with acetylacetone. The resultant products on cyclisation have yielded substituted indenes.

It appears that the Michael condensation on β-nitrostyrenes has not been studied much (Kohler and Engelbrecht, *J. Amer. Chem. Soc.*, 1919, **41**, 764). Condensations of β-nitrostyrene and 3 : 4-dimethoxy-β-nitrostyrene with ethyl acetoacetate as well as with acetylacetone have been effected in presence of sodium ethoxide in ethanol to form compounds (I) and (II) respectively. It has been observed that even 1/20 molar proportion of sodium ethoxide is quite sufficient to effect condensation in some cases. Duration of reaction markedly affects the yield of the desired product. With increase in temperature of condensation or with increase in time of reaction, side products predominate and the resultant products are tarry, noncrystallisable mass.



(I)



(II)

The above ketones have been cyclised easily in presence of concentrated H_2SO_4 or a mixture of H_3PO_4 and H_2SO_4 to form indenes. Such indenes possessing a nitromethyl group cannot be otherwise prepared easily.

*Experimental

Ethyl α -(2-Phenylnitroethyl)acetoacetate (I: X=H).—To a mixture of β-nitrostyrene (30 g.) and ethyl acetoacetate (30 g.) in ethanol (125 c.c.), cooled to 5°, was added dropwise with stirring a solution of NaOEt (0.2 g. Na in 10 c.c. ethanol) under cooling. The temperature immediately began to rise, which was controlled at 5-10°. After the addition was over (20 minutes), white crystals began to separate from the clear solution. Stirring was continued for another 25 minutes and the thick mass was poured into ice-water (800 g.) containing acetic acid (15 c.c.). The separated solid was filtered, washed with water, and subsequently washed with ice-cold ethanol (75 c.c.). The residual solid was dried in air. It was crystallised from petroleum ether (60-80°) in fine, colorless needles, m.p. 76-78°, yield 45 g. (Found : C, 60.2 ; H, 6.1 ; N, 4.9. $C_{14}H_{16}O_5N$ requires C, 60.4 ; H, 5.8 ; N, 5.03%). It is highly soluble in ethanol and does not exhibit any characteristic colour with $FeCl_3$.

* All m.p.s. are uncorrected.

1-Nitromethyl-2-carboxy 3-methylindene.—The above crude keto-ester (15 g.) was dissolved in H_2SO_4 (conc., 120 c.c.) at 10-15° and kept at 20-22° for 3 hours. The mass was then poured on ice, the precipitated solid filtered, and washed with water. The crude mass was then dissolved in cold dilute NH_3, charcoaled, filtered, and acidified with HCl to liberate the acid; yield 40 g. It was crystallised from ethanol in light yellow needles, m.p. 188°. (Found: C, 61.7; H, 5.1; N, 5.8. $C_{12}H_{11}O_4N$ requires C, 61.8; H, 4.7; N, 6.0%). On oxidation with alkaline $KMnO_4$ it yielded phthalic acid.

It was esterified with ethanol and dry HCl gas. The ester crystallised from ethanol in light yellow cubes, m.p. 85°. (Found: C, 64.4; H, 5.8; N, 5.49. $C_{14}H_{15}O_4N$ requires C, 64.36; H, 5.78; N, 5.37%).

Ethyl α-[2-(3′: 4′-Dimethoxyphenyl)-nitroethyl]-acetoacetate (I: X=OMe-3′: 4′).—A mixture of 3: 4-dimethoxy-β-nitrostyrene (10.5 g.) and ethyl acetoacetate (7.5 g.) in ethanol (200 c.c.) was treated with NaOEt (0.1 g. Na in 10 c.c. ethanol) in the preceding manner; yield 12 g. It was crystallised from benzene-petroleum ether in colorless needles, m.p. 105-106°. (Found: C, 56.2; H, 5.88. $C_{16}H_{21}O_7N$ requires C, 56.6; H, 6.19%).

1-Nitromethyl-2-ethoxycarbonyl-3-methyl-5: 6-dimethoxyindene.—The above keto-ester (9 g.) was cyclised in a mixture of H_2SO_4 (conc., 30 c.c.) and H_3PO_4 (60 c.c.). The reaction product was an ester and not an acid in this case. It was crystallised from ethanol in light yellow needles, m.p. 149-50°, yield 5 g. (Found: C, 59.6; H, 5.8. $C_{16}H_{19}O_6N$ requires C, 59.81; H, 5.91%).

α-(2-Phenylnitroethyl)-acetylacetone (II: X=H).—A mixture of β-nitrostyrene (7.5 g.) and acetylacetone (5.5 g.) in ethanol (30 c.c.) was condensed in presence of NaOEt (from 0.1 g. Na) at 5-10°. It was crystallised from ethanol in colorless needles, m.p. 112-13°, yield 11 g. (Found: C, 62.9; H, 5.85; N, 5.76. $C_{13}H_{15}O_4N$ requires C, 62.65; H, 6.02; N, 5.62%).

1-Nitromethyl-2-acetyl-3-methylindene.—The above compound was cyclised in H_2SO_4 (conc.). It was crystallised from ethanol in light yellow needles, m.p. 103-104°. (Found: C, 67.42; H, 5.67; N, 6.16. $C_{13}H_{13}O_3N$ requires C, 67.53; H, 5. 62; N, 6.06%).

α- 2-(3′: 4′-Dimethoxyphenyl)nitroethyl-acetylacetone (II: X=OMe-3′: 4′).—3: 4-Dimethoxy-β-nitrostyrene (5 g.) was condensed with acetylacetone (2.5 g.) in ethanol (80 c.c.) in presence of NaOEt (out of 0.2 g. Na). It was crystallised from a large volume of ethanol in needles, m.p. 184-86°. (Found: C, 57.84; H, 6.11. $C_{15}H_{19}O_6N$ requires C, 58.25; H, 6.14%).

1-Nitroethyl-2-acetyl-3-methyl-5: 6-dimethoxyindene.—The above compound was cyclised in H_2SO_4 (conc.). It was crystallised from ethanol in colorless needles, m.p. 135-37°. (Found: C, 61.5; H, 5.88. $C_{15}H_{17}O_5N$ requires C, 61.85; H, 5.84%).

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STUDIES ON SYNTHETIC ESTROGENS. PART II

BY H. SINGH AND R. S. KAPIL*

Several 2-*p*-chloro- and 2-*p*-bromo-benzoylbenzofurans have been synthesised as possible estrogenic compounds.

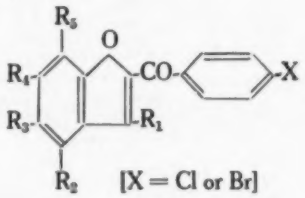
In a recent communication (Singh and Kapil, *J. Org. Chem.*, 1959, **24**, 2064) preparation of a number of 2-*p*-anisoylbenzofurans as possible estrogens has been described. The studies have now been extended to certain 2-*p*-chloro- and 2-*p*-bromo-benzoylbenzofuran derivatives. All of them have been prepared by condensing potassium salts of the appropriate hydroxy-ketones with *p*-chloro- and *p*-bromo-phenacyl bromides in ethanol (vide Tables I and II).

The substituted benzofurans, prepared, are colorless crystalline solids, insoluble in water and alkalies, and soluble in ethanol and acetic acid. It is noteworthy that 3-methyl-substituted compounds are much less soluble than the corresponding 3-ethylbenzofurans. The yields of the 3-methyl-substituted benzofurans, in general, are better than the corresponding 3-ethyl-substituted compounds.

EXPERIMENTAL**

o-Hydroxyketones required in the synthesis were prepared through the Fries migration (*Ber.*, 1908, **41**, 4271).

2-*p*-Chloro- and 2-*p*-bromo-benzoylbenzofurans were prepared by the procedure described earlier (Singh and Kapil, *loc. cit.*).



[X = Cl or Br]

TABLE I

2-p-Chlorobenzoylbenzofurans.

No.	R_1.	R_2.	R_3.	R_4.	R_5.	M.P.	Formula.	% Halogen Found	% Halogen Calc.
1.	Me	H	H	Cl	H	142°	$C_{16}H_{10}O_2Cl_2$	Cl: 23.1	23.2
2.	„	H	Cl	H	H	125°	$C_{16}H_{10}O_2Cl_2$	Cl: 23.0	23.2
3.	„	H	Me	H	Br	190°	$C_{17}H_{12}O_2ClBr$	Cl + Br: 31.7	31.8
4.	„	Cl	H	H	Cl	156°	$C_{16}H_9O_2Cl_3$	Cl: 31.1	31.3
5.	„	H	Cl	Cl	H	177°	$C_{16}H_9O_2Cl_3$	Cl: 31.2	31.3
6.	„	H	Br	H	Cl	214°	$C_{16}H_9O_2Cl_2Br$	Cl + Br: 39.0	39.3
7.	„	H	Cl	H	Br	120°	$C_{16}H_9O_2Cl_2Br$	Cl + Br: 39.1	39.3
8.	Et	H	Br	H	Cl	140°	$C_{17}H_{11}O_2Cl_2Br$	Cl + Br: 37.8	37.9

N.B. All the compounds were recrystallised from AcOH-EtOH excepting No. 8, which was recrystallised from EtOH.

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** All melting points are uncorrected.

TABLE II

2-p-Bromobenzoylbenzofurans.

No.	R_1	R_2	R_3	R_4	R_5	M.P.	Formula.	% Halogen. Found.	Calc.
1.	Me	H	Me	H	H	145°	$C_{17}H_{13}O_2Br$	Br: 24.1	24.3
2.	„	H	H	Cl	H	132°	$C_{16}H_{10}O_2ClBr$	Cl + Br: 32.9	33.0
3.	„	H	Cl	H	H	130°	$C_{16}H_{10}O_2ClBr$	Cl + Br: 32.8	33.0
4.	„	H	Br	H	H	125°	$C_{16}H_{10}O_2Br_2$	Br: 40.4	40.6
5.	„	H	Me	H	Br	186°	$C_{17}H_{12}O_2Br_2$	Br: 39.1	39.2
6.	„	H	Cl	Cl	H	167°	$C_{16}H_9O_2Cl_2Br$	Cl + Br: 39.2	39.3
7.	„	H	Br	H	Cl	173°	$C_{16}H_9O_2ClBr_2$	Cl + Br: 45.5	45.6
8.	Et	H	Cl	H	H	115°	$C_{17}H_{12}O_2ClBr$	Cl + Br: 31.6	31.7
9.	„	H	Br	H	H	175°	$C_{17}H_{12}O_2Br_2$	Br: 39.0	39.2
10.	„	H	Br	H	Cl	160°	$C_{17}H_{11}O_2ClBr_2$	Cl + Br: 44.0	44.1

N.B. Compounds No. 1—7 were recrystallised from AcOH-EtOH and the rest from EtOH.

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CHEMICAL CONSTITUENTS OF *DURANTA REPENS* LINN

By R. S. Kapil*

Two crystalline compounds, identified as β-sitosterol and ursolic acid, have been isolated from the fruits of *Duranta repens* Linn.

Duranta repens Linn (syn. *Duranta plumieri* Jacq.) (Family Verbenaceae) is an erect shrub found throughout India and is cultivated in gardens as a hedge plant. The fruits are nonedible and are reported to contain an alkaloid (Bootsma, *Meded. Lands Plantentuin*, Java, 1899, **31**, 122) and a fatty oil (Kafuku and Hata, *J. Chem. Soc., Japan*, 1936, **57**, 727). The juice of the macerated fruits has also been found to be an effective laryicide (Manson, *J. Malar. Inst., India*, 1939, **2**, 85).

In view of the reported insecticidal properties of this plant (Chopra, Badhwar and Ghosh, "Poisonous Plants of India", 1949, p. 57) it was considered desirable to undertake a detailed study of the fruits. The air-dried, powdered fruits on extraction with petroleum ether (b.p. 60-80°) yielded a mixture of a substance (A) and a waxy material. This was hydrolysed with ethanolic KOH (10%) and the unsaponified material was chromatographed over alumina using petroleum ether and benzene-chloroform as successive eluents. The benzene-chloroform fractions on concentration and crystallisation from methanol afforded a pure substance (A), m.p. 136°, identified as β-sitosterol.

The defatted powdered fruit was then extracted with ethyl acetate, which on concentration yielded a pale yellow amorphous powder. This on purification and repeated crystallisation from ethanol and acetone gave the substance (B), m.p. 278°. Comparison of (B) and its various derivatives with those of ursolic acid indicates its identity with that of the latter (Table I). Final confirmation was achieved by undepressed mixed m.p. with an authentic sample.

TABLE I

Compound.	Formula.	Ursolic acid†. M.P.	Ursolic acid†. $[\alpha]_D$ ($CHCl_3$).	Ursolic acid from *Duranta repens* Linn. M.P.	Ursolic acid from *Duranta repens* Linn. $[\alpha]_D$ ($CHCl_3$).
Ursolic acid	$C_{30}H_{48}O_3$	286-87°	+70°	278°	+70°.1
Acetylursolic acid	$C_{32}H_{50}O_4$	286-87°		279°	
Methyl ursolate	$C_{31}H_{50}O_3$	171°	+69°	168°	+68°.0
Acetylmethyl ursolate	$C_{33}H_{52}O_4$	246-47°		243°	

† Simonsen and Ross, "The Terpenes", 1957, vol. V, p. 114.

EXPERIMENTAL

The powdered, air-dried fruits (5 kg.) were extracted first with hot petroleum ether and then with ethyl acetate.

Petroleum Ether Extract

The pale yellow petroleum ether extract was concentrated (weighed 100 g.) and then hydrolysed by refluxing on a water bath for 12 hours with EtOH-KOH (10%). The excess of ethanol

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was removed under vacuum, diluted with water and repeatedly extracted with petroleum ether. The residue left after removal of the solvent (weighed 30 g.) was dissolved in minimum amount of petroleum ether and chromatographed over alumina (900 g.), using petroleum ether and benzene-chloroform (3 : 2) as successive eluents. The forerun with petroleum ether was waxy in nature; from the benzene-chloroform fractions β-sitosterol was isolated, which crystallised from methanol in colorless plates (5 g.), m.p. 136°, $[\alpha]_D$ −34°.5 (chloroform). It develops a pink coloration changing to blue and then green in the Liebermann-Burchard reaction and shows no depression in m.p. on admixture with an authentic sample. (Found : C, 84.14; H, 11.98. Calc. for $C_{29}H_{50}O$: C, 84.05; H, 12.07%).

β-Sitosterol Acetate.—β-Sitosterol (0.5 g.) on heating with acetic anhydride (10 c.c.) and fused sodium acetate (0.5 g.) for 2 hours furnished the acetate (0.42 g.). It was crystallised from ethanol in colorless needles, m.p. 126°, $[\alpha]_D$ −41°.3 (chloroform). (Found : C, 81.32; H, 11.78. Calc. for $C_{31}H_{52}O_2$: C, 81.57; H, 11.40%).

Ethyl Acetate Extract

This extract on concentration afforded a yellow amorphous residue (37.5 g.), which on decolorisation with charcoal and several crystallisations from ethanol and acetone furnished ursolic acid in colorless needles, m.p. 278°, $[\alpha]_D$ +70°.1 (chloroform). It develops a violet coloration, which immediately changes to blue and finally turns green in the Liebermann-Burchard reaction. Mixed m.p. determination with an authentic sample showed no depression. (Found : C, 78.58; H, 10.82. Calc. for $C_{30}H_{48}O_3$: C, 78.72; H, 10.52%).

Acetylursolic acid was prepared by heating ursolic acid with acetic anhydride and fused sodium acetate. It was crystallised from ethanol in colorless needles, m.p. 279°, $[\alpha]_D$ + 68°.0 (chloroform). (Found : C, 76.72; H, 10.34. Calc. for $C_{32}H_{50}O_4$: C, 77.10; H, 10.04%).

Methyl ursolate was prepared by treating ursolic acid with an ethereal solution of diazomethane. It was crystallised from methanol in colorless needles, m.p. 168°. (Found : C, 78.74; H, 10.28. Calc. for $C_{31}H_{50}O_3$: C, 79.14; H, 10.63%).

Acetylmethyl ursolate was prepared by heating methyl ursolate with acetic anhydride and fused sodium acetate. It was crystallised from acetone in colorless needles, m.p. 243°. (Found : C, 77.03; H, 10.43. Calc. for $C_{33}H_{52}O_4$: C, 77.32; H, 10.15%).

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STUDIES IN THE HYDROXYANTHRACENE SERIES. PART III.* SYNTHESIS OF SOME HETEROCYCLIC COMPOUNDS FROM 1-ANTHROL

BY N. H. SHAH AND SURESH SETHNA

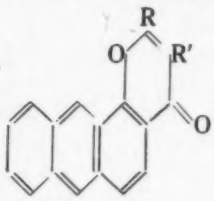
Syntheses of 2′-methyl- and 2′-phenyl-1:2-anthra-γ-pyrone, 2′-phenyl-2′:3′-dihydro-1:2-anthra-γ-pyrone and 3-methylanthra-[1:2-b]furan have been described.

The reactions of 1-anthrol, described earlier (Lele, Shah and Sethna, *J. Org. Chem.*, 1956, **21**, 1293), have been extended to the synthesis of anthra-γ-pyrone and anthra-furan derivatives.

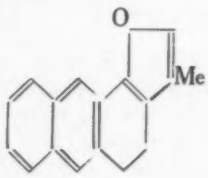
2-Acetyl-1-anthrol on the Kostanecki-Robinson acetylation furnished 2′-methyl-3′-acetyl-1:2-anthra-γ-pyrone (I a). This on heating with dilute ethanolic sodium carbonate solution afforded 2′-methyl-1:2-anthra-γ-pyrone (I b), which yielded a styryl derivative with benzaldehyde, and 2-acetyl-1-anthrol on hydrolysis. The same ketone on the Kostanecki-Robinson benzoylation gave 2′-phenyl-3′-benzoyl-1:2-anthra-γ-pyrone (I c), which on heating with dilute ethanolic sodium carbonate solution furnished 2′-phenyl-1:2-anthra-γ-pyrone (I d). The γ-pyrone derivatives (I b and I d) were also obtained by refluxing 1-anthrol with ethyl acetoacetate and ethyl benzoylacetate respectively in diphenyl ether solution according to the method of Desai *et al.* (*J. M. S. Univ., Baroda*, 1955, **4**, No. 2, p. 1).

2-Acetyl-1-anthrol on condensation with benzaldehyde in presence of alkali yielded 2-hydroxyanthrylstyryl ketone. It afforded an acetyl derivative. The styryl ketone was isomerised by heating its ethanolic solution with dilute sulphuric acid to 2′-phenyl-2′:3′-dihydro-1:2-anthra-γ-pyrone. This on dehydrogenation with selenium dioxide gave 2′-phenyl-1:2-anthra-γ-pyrone (I d), identified by direct comparison with the product described above.

2-Acetyl-1-anthrol on condensation with ethyl bromoacetate furnished ethyl 2-acetyl-1-anthroxyacetate, which on hydrolysis gave 2-acetyl-1-anthroxyacetic acid. On heating with sodium acetate and acetic anhydride it afforded 3-methylanthra-[1:2-b]furan(II). The results of analysis and the absence of a free acetyl group in this compound indicate that the meso position is not involved in the ring closure. Further, 1-anthroxyacetic acid remained unchanged on subjecting it to the action of sodium acetate and acetic anhydride.



(I)



(II)

(a) R = Me; R′ = COMe.
(b) R = Me; R′ = H.
(c) R = Ph; R′ = COPh.
(d) R = Ph; R′ = H.

* Part II, *J. Org. Chem.*, 1959, **24**, 1783.

EXPERIMENTAL*

2'-Methyl-3'-acetyl-1:2-anthra-γ-pyrone (I a).—2-Acetyl-1-anthrol (1 g.) was heated with freshly fused sodium acetate (3 g.) and acetic anhydride (6 c.c.) in an oil bath at 180° for 8 hours. The product obtained on working up the reaction mixture was crystallised from ethanol (charcoal) in light yellow needles, m.p. 196-97°. (Found : C, 79.9; H, 4.5. $C_{20}H_{14}O_3$ requires C, 79.5; H, 4.6%).

2'-Methyl-1 : 2-anthra-γ-pyrone (I b).—The above γ-pyrone (0.5 g.) in 50% ethanol (50 c.c.) was refluxed with sodium carbonate (2 g.) for 2 hours. The product obtained was crystallised from dilute ethanol (charcoal) in yellowish brown needles, m.p. 210-11.° (Found : C, 83.5; H, 5.0. $C_{18}H_{12}O_2$ requires C, 83.1; H, 4.6%). On refluxing with EtOH-KOH on a steam bath it breaks down into 2-acetyl-1-anthrol.

The same product was obtained when 1-anthrol (0.99 g.) in hot diphenyl ether was refluxed for 2 hours with ethyl acetoacetate (0.65 g.) and the solution diluted on cooling with petroleum ether.

2'-Styryl-2 : 1-anthra-γ-pyrone.—The above γ-pyrone (0.1 g.) was dissolved in ethanol (5c.c.) and treated successively with benzaldehyde (0.1 g.) and a solution of sodium ethoxide (prepared from 0.1 g. of sodium). The greenish yellow crystalline product, which separated on keeping overnight, was filtered and recrystallised from dilute ethanol (charcoal) in yellow shining needles, m.p. 216°. (Found : C, 85.8 ; H, 4.6. $C_{25}H_{16}O_2$ requires C, 86.2 ; H, 4.6%).

2'-Phenyl-3'-benzoyl-1-anthra-γ-pyrone (I c).—2-Acetyl-1-anthrol (1 g.) was heated with freshly fused sodium benzoate (1.5 g.) and benzoic anhydride (5 g.) in an oil bath at 180° for 8 hours. The reaction mixture was then treated repeatedly with hot water and sodium bicarbonate, and the residue was crystallised from ethanol (charcoal) in small yellow needles, m.p. 222°. (Found : C, 84.4 ; H, 4.1. $C_{30}H_{18}O_3$ requires C, 84.5 ; H, 4.2%).

2'-Phenyl-1 : 2-anthra-γ-pyrone (I d).—The above γ-pyrone (0.5 g.) in 50% ethanol (50 c.c.) was refluxed with sodium carbonate (2 g.) for 2 hours. The product obtained was crystallised from ethanol (charcoal) in yellow needles, m.p. 215-16°. (Found : C, 85.8 ; H, 4.6. $C_{23}H_{14}O_2$ requires C, 85.7 ; H, 4.4%).

The same product was obtained when 1-anthrol (0.48 g.) in hot diphenyl ether was refluxed for 2 hours with ethyl benzoylacetate (0.48 g.) ; the solution on cooling was diluted with petroleum ether.

2-Hydroxyanthrylstyryl Ketone.—To a mixture of 2-acetyl 1-anthrol (1.2 g.) and benzaldehyde (2. c.c.) in ethanol (50 c.c.) KOH solution (2.5 g. in 5 c.c. water) was added in small lots. The air was removed by bubbling nitrogen through the solution ; the flask was corked and kept for 2 days at room temperature. The product separating on dilution of the reaction mixture was crystallised from ethanol in reddish brown needles, m.p. 207°. (Found : C, 84.8 ; H, 4.8. $C_{23}H_{16}O_2$ requires C, 85.2 ; H, 4.9%). It develops a reddish brown coloration with alcoholic ferric chloride.

The *acetyl derivative* was prepared by heating the styryl ketone (0.1 g.) with acetic anhydride (1 c.c.) and freshly fused sodium acetate (0.1 g.) on a steam bath for 5 hours. It was crystallised from ethanol (charcoal) in small yellowish needles, m.p. 180-81°. (Found : C, 82.3 ; H, 5.2. $C_{25}H_{18}O_3$ requires C, 82.0 ; H, 4.9%).

* All melting points are uncorrected.

*2'-Phenyl-2' : 3'-dihydro-*1 : 2-*anthra-*γ*-pyrone.*—The above hydroxyanthrylstyryl ketone (0.1 g.) in ethanol (100 c.c.) was refluxed on a steam bath for 48 hours with 10% H_2SO_4 (10 c.c.). The product separating on dilution with water was crystallised from chloroform, m.p. 231°. (Found : C, 84.8 ; H, 4.8. $C_{23}H_{16}O_2$ requires C, 85.2 ; H, 4.9%).

A mixture of this substance (0.1 g.), selenium dioxide (0.2 g.), and amyl alcohol (10 c.c.) was heated under reflux at 150° for 8 hours ; the reaction mixture was then filtered hot. On evaporation of the amyl alcohol the product obtained was crystallised from ethanol in light yellow needles; m.p. and mixed m.p. with 2'-phenyl-1 : 2-anthra-γ-pyrone was 215-16°.

*Ethyl 2-Acetyl-*1*-anthroxyacetate.*—A mixture of 2-acetyl-1-anthrol (0.5 g.), ethyl bromoacetate (0.5 c.c.), and anhydrous potassium carbonate (3 g.) was refluxed in acetone solution for 4 hours. The product obtained on removal of acetone was crystallised from dilute ethanol (charcoal) in golden yellow needles, m.p. 108-109°. (Found : C, 74.9 ; H, 5.3. $C_{20}H_{18}O_4$ requires C, 74.5 ; H, 5.6%).

*2-Acetyl-*1*-anthroxyacetic Acid.*—The above ester (0.5 g.) was heated with 2% NaOH solution (50 c,c.) at 50° in a water bath till the ester dissolved. The solution was then filtered hot. The product obtained on acidification of the filtrate was crystallised from dilute acetic acid (charcoal) in yellow needles, m.p. 161-62° (efferv.). (Found : C, 73.1 ; H, 4.5. $C_{18}H_{14}O_4$ requires C, 73.5 ; H, 4.8%).

3-Methylanthra-(1 : 2-b)*furan* (II).—A mixture of the above acid (0.1 g.), acetic anhydride (2 c.c.), and freshly fused sodium acetate (0.3 g.) was refluxed for 30 minutes. The product obtained on pouring it in water was crystallised from ethanol (charcoal) in light yellow needles, m.p. 104°. (Found : C, 87.3 ; H, 5.6. $C_{17}H_{12}O$ requires C, 87.9 ; H, 5.2%).

1-*Anthroxyacetic Acid.*—A mixture of 1-anthrol (1 g.), ethyl bromoacetate (1 c.c.), and anhydrous potassium carbonate (3 g.) was refluxed in acetone solution for 7 hours. An oil was obtained on removal of acetone. This was hydrolysed in ethanolic solution with KOH (2 g. in 5 c.c. water) by heating on a steam bath for 2 hours. The product obtained was purified through sodium bicarbonate treatment and crystallised first from dilute ethanol (charcoal) and then from benzene in colorless needles, m.p. 190-91°. (Found : C, 76.3 ; H, 4.9. $C_{16}H_{12}O_3$ requires C, 76.2 ; H, 4.8%).

The acid (0.1 g.) was refluxed with sodium acetate (0.3 g.) and acetic anhydride (2 c.c.) for 30 minutes. The original acid was obtained on working up the reaction mixture.

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INTERFERENCE CORRECTIONS FOR THE GROUPINGS CONTAINING NITROGEN

By A. M. Talati

The group parachor values for the groups $(C)_2NH$ and $(C)_3N$, and the interference correction for the grouping C—N—C are derived. "Atomic parachor" of nitrogen and the values of the interference corrections for the groupings C—N—N, N—C—N, and N—N—N are suggested.

Gibling (*J. Chem. Soc.*, 1943, 146, 151) has suggested that the values of the interference corrections (I.C.) for the groupings C—C—N and C—N—C should be 2.2 and 3.1 respectively. The value of I.C. for the grouping C—C—N was assumed by him from a comparison of the values of I.C. for the groupings C—C—C and C—C—O. Although the value for the grouping C—N—C was derived by him by the method used for the calculation of the interference correction for the grouping C—C—C (*ibid.*, 1941, 299), the parachor values used therein appear to have been obtained on certain "assumptions". The present author (this *Journal*, 1955, **32,** 799) has shown that the values of I.C. for the groupings C—C—C and C—C—N are of the same order and that the value of the I.C. for the grouping C—C—X will be the same for the elements of the same period in the Periodic Table. Hence it is of importance to know the value of I.C. for the groupings containing nitrogen.

In Table I are presented the compounds, parachor values of which are known and from which R. P. values and R. P. values corrected for I.C. due to C—C—C and C—C—N are calculated for the groups shown therein.

TABLE I

Compounds.	$[P]_{obs.}$	Group or compound.	R. P.			Group parachor (ideal)
			Calc.	Corr.	Diff.	
Dimethyl amine	139.7	$(CH_3)_2NH$	139.5	139.5	..	..
Diethyl amine	219.6	(C) CH_2NH CH_2(C)	108.7	113.1	26.4	115.3
Dipropyl[2] amine	296.2	$(C)_2CHNH$ $CH(C)_2$	73.5	86.7	26.4	88.9
Dibutyl[2] amine	374.3					

The difference between the successive parachor values is constant, *i.e.*, 26.4, which is equal to 2×13.2. Thus the difference indicates the replacement of two hydrogen atoms. Hence, if we subtract the ideal group parachor values of $CH_3(N)$, $(C)CH_2(N)$ and/or $(C)_2CH(N)$ from the above groups, we shall get the value of (C)NH(C) (uncorrected for C-N-C) as 29.1. Now the group parachor value for the group $(C)NH_2$ has been found by the author to be 44.5. Hence the difference between the parachor values of $(C)NH_2$ and (C)NH(C) will be 15.4. This indicates that if the parachor value of hydrogen is taken as 13.2, the value of I.C. for C—N—C will be 2.2, *i.e.*, same as for C—C—C and C—C—N. This result indicates that nitrogen atom, whether placed at the end as in C—C—N or in the middle as in C—N—C, has the same interference effect.

Ideal group parachor values for these groups are also presented in Table I. Ideal group parachor value for the group $(C)_3CNHC(C)_3$ will be 62.5 and that for (C)NH(C) will be 31.3 [Gibling's value for (C) NH(C) is 35.1].

These results lead us to an idea that C and N atoms behave similarly as regards interference. If this is so, the same value of I.C. will be obtained not only for the groups C—C—N and C—N—C, but also for the groups C—N—N, N—C—N, and N—N—N. It is not possible, however, to derive these values by the present method. Hence by an indirect method the values of these groups may be calculated on the assumption that the value of I.C. for different groups containing C and N is the same, namely, 2.2. For that purpose it will be necessary to calculate the "atomic parachor" value of N.

Atomic Parachor of Nitrogen

Gibling (*J. Chem. Soc.*, 1941, 299) has mainly worked on the evaluation of the group parachor values and has regarded atomic parachor values derived by the usual method as unsatisfactory. He (*ibid.*, 1945, 236) has, however, calculated the atomic constants for carbon and hydrogen on the basis of the interference concept. He has not so far attempted to calculate the atomic constants for other atoms. For the purpose of arriving at the value of I.C. for C—N—C, he has derived the group parachor values for the groups $(C)NH_2$, $(C)_2NH$, and $(C)_3N$. These values may be utilised to derive the atomic parachor value of nitrogen as shown in Table II.

TABLE II

Group.	Ideal R.P. (Gibling)	Diff.	Ideal R.P. (Talati)	Diff.
$(C)NH_2$	47.9	..	44.5	..
$(C)_2NH$	35.1	12.8	31.3	13.2
$(C)_3N$	22.3	12.8	18.1	13.2

The difference between the successive groups is constant and is 12.8. This indicates that the ideal value of hydrogen in nitrogen compounds may be taken as 12.8. From these values the atomic parachor (ideal) for nitrogen may be calculated as 22.3, I. C. for C—N—C being taken as 3.1.

The author's values for the groups $(C)NH_2$, $(C)_2NH$, and $(C)_3N$ are also shown in Table II. The group parachor value for the group $(C)_3N$ is derived from the known parachor value of trimethyl amine as 11.5. Hence the ideal R.P. for the group will be $11.5+6.6=18.1$.

The difference between the successive ideal R.P. values is constant, namely, 13.2. This indicates that the parachor value of hydrogen in nitrogen compounds is the same as the parachor value of hydrogen in the hydrocarbons. From these results the ideal atomic parachor value for nitrogen is calculated as 18.1.

The values derived from those of present author have an advantage over those obtained by using Gibling's values. Thus the author's considerations lead to an idea that the values of I.C. for C—N—N, N—C—N, and N—N—N should be same as those for C—C—N-and C—N—C, *i.e.*, 2.2. Although Gibling obtained different values for I.C. of C—C—N and C—N—C (2.4 and 3.1 respectively), he assumed that in the case of polynitrogen compounds nitrogen atoms produced interferences of the same order as those given by carbon atoms. This assumption contradicts, however, the values obtained by him for C—C—N and C—N—C. Further, his results lead to different atomic parachor values of hydrogen in hydrocarbons and in nitrogen compounds.

Using the author's values, the ideal R.P. values, and uncorrected group parachor values for various groups containing N are calculated as follows (Table III).

TABLE III

Group.	Ideal R.P.	Group parachor (uncorrected).
(N) NH_2	44.5	44.5
(C) NH (N)	31.3	29.1
(C) N $(N)_2$	18.1	11.5
$(C)_2N(N)$	18.1	11.5

The author takes this opportunity of expressing his gratefulness to Dr. M. D. Avasare, Principal, J. and J. College of Science, Nadiad, and to Prof. S. M. Sethna, Prof. R. L. Desai, and to Dr. J. S. Dave for their interest in the work.

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BENZYLTHIOUREAS. PART IV

BY S. P. KHARIDA, P. R. PATHAN, P. S. SATPANTHI AND J. J. TRIVEDI

Several *N'*-benzyl-*N''*-aryl/2-biphenylyl /2-thiazolyl /2-thiazolinyl /2-pyridyl- and β-hydroxyethyl-thioureas have been prepared.

Aryl ureas and thioureas are known to exhibit bacteriostatic activity (Beaver *et al.*, *J. Amer. Chem. Soc.*, 1957, **79,** 1236; Buu-Hoï *et al.*, *J. Chem. Soc.*, 1958, 2815; Doub *et al.*, *J. Amer. Chem. Soc.*, 1958, **80,** 2205). Important bacteriostats contain thiazole and pyridine rings. Some thiazoline derivatives also exhibit bacteriostatic activity (Gardener *et al.*, *J. Org. Chem.*, 1955, **20,** 976; Mizzoni *et al.*, *J. Amer. Chem. Soc.*, 1958, **80,** 3471). 2-Biphenylylthiourea exhibits the same order of toxicity to rats as α-naphthylthiourea (U.S. Patent 2, 390,848; *Chem. Abs.*, 1946, **40,** 1966). Several benzylthioureas also show bacteriostatic and fungitoxic activity (Trivedi *et al.*, this *Journal*, 1956, **33,** 423; 1958, **35,** 657; McKay *et al.*, *J. Amer. Chem. Soc.*, 1959, **81,** 4328).

Thus we found it of considerable interest to study thioureas containing aryl, hetero, and other groups in addition to a substituted benzyl group. We have prepared the following types of unsymmetrical thioureas by the action of appropriate amine on substituted benzyl *iso*thiocyanates:

(*a*)	*N'*-	(subst.)	-benzyl-*N''*-aryl-		thioureas	Table I
(*b*)	*N'*	,,	,,	*N''* (2-pyridyl)-	,,	II
(*c*)	*N'*	,,	,,	*N''* (2-thiazolinyl)-	,,	III
(*d*)	*N'*	,,	,,	*N''* (2-thiazolyl)-	,,	IV
(*e*)	*N'*	,,	,,	*N''* (2-biphenylyl)-	,,	V
(*f*)	*N'*	,,	,,	*N''* (β-hydroxyethyl)-	,,	VI

EXPERIMENTAL

2-Aminothiazoline was prepared from monoethanolamine by the method of Raiziss and Clemence (*J. Amer. Chem. Soc.*, 1941, **63,** 3125). 2-Aminothiazole and 2-aminopyridine were of Eastman's practical grade. Substituted benzyl *iso*thiocyanates were prepared as described previously (Trivedi *et al.*, *loc. cit.*). Unsymmetrical thioureas were prepared by the action of appropriate amines on substituted benzyl *iso*thiocyanates in ethanolic solution as described previously (*loc. cit.*). Thioureas were crystallised from ethanol.

TABLE I

$X\text{-}C_6H_4CH_2NHCSNH\text{-}C_6H_4\text{-}R$.

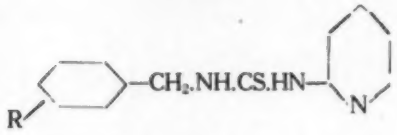
Compounds. (R=)	M.P.	Formula.	% Sulphur. Found.	Calc.	Compounds. (R=)	M.P.	Formula.	% Sulphur. Found.	Calc.
		X=H.					X=*o*-Cl.		
					H	176°	$C_{14}H_{13}N_2ClS$	11.8	11.6
o-Cl	113°	$C_{14}H_{13}N_2ClS$	11.7	11.6	*o*-Cl	130°	$C_{14}H_{12}N_2Cl_2S$	10.5	10.3
m-Cl	117°	,,	11.4	11.6	*m*-Cl	158°	,,	10.2	10.3
p-Cl	118°	,,	11.8	11.6	*p*-Cl	175°	,,	10.4	10.3
o-Br	143°	$C_{14}H_{13}N_2BrS$	10.2	10.0	*o*-Br	132°	$C_{14}H_{12}N_2ClBrS$	9.2	9.0
m-Br	118°	,,	9.8	10.0	*m*-Br	130°	,,	9.3	9.0
p-Br	132°	,,	10.3	10.0	*p*-Br	162°	,,	8.9	9.0
o-Me	131°	$C_{15}H_{16}N_2S$	12.3	12.5	*o*-Me	183°	$C_{15}H_{15}N_2ClS$	11.1	11.0
m-Me	116°	,,	12.7	12.5	*m*-Me	117°	,,	11.3	11.0
p-Me	120°	,,	12.6	12.5	*p*-Me	142°	,,	10.8	11.0
o-OMe	140°	$C_{15}H_{16}ON_2S$	11.9	11.8	*o*-OMe	153°	$C_{15}H_{15}ON_2ClS$	10.2	10.4
					p-OMe	170°	,,	10.6	10.4

TABLE I (*contd.*)

Compunds. (R=)	M.P.	Formula.	% Sulphur. Found.	Calc.
		X=*m*-Cl.		
H	91°	$C_{14}H_{13}N_2S$	11.7	11.6
o-Cl	80°	$C_{14}H_{12}N_2Cl_2S$	10.5	10.3
m-Cl	85°	,,	10.4	10.3
p-Cl	125°	,,	10.2	10.3
p-Br	126°	$C_{14}H_{12}N_2ClBrS$	9.2	9.0
o-Me	93°	$C_{15}H_{15}N_2ClS$	11.1	11.0
m-Me	118°	$C_{15}H_{15}N_2ClS$	11.2	11.0
p-Me	95°	,,	10.9	11.0
o-OMe	151°	$C_{15}H_{15}ON_2ClS$	10.5	10.4
p-OMe	183°	,,	10.6	10.4
		X=*p*-Cl.		
H	136°	$C_{14}H_{13}N_2ClS$	11.7	11.6
o-Cl	142°	$C_{14}H_{12}N_2Cl_2S$	10.2	10.3
m-Cl	146°	,,	10.5	10.3
p-Cl	185°	,,	10.4	10.3
o-Br	161°	$C_{14}H_{12}N_2ClBrS$	9.2	9.0
m-Br	164°	,,	8.8	9.0
p-Br	182°	,,	9.3	9.0
o-Me	118°	$C_{15}H_{15}N_2ClS$	11.3	11.0
m-Me	145°	,,	10.9	11.0
p-Me	162°	,,	11.2	11.0
o-OMe	140°	$C_{15}H_{15}ON_2ClS$	10.5	10.3
p-OMe	132°	,,	10.4	10.3
		X=*p*-Br.		
H	142°	$C_{14}H_{13}N_2BrS$	10.2	10.0
o-Cl	149°	$C_{14}H_{12}N_2ClBrS$	9.1	9.0
m-Cl	95°	,,	8.9	9.0
p-Cl	185°	,,	9.0	9.0
p-Br	186°	$C_{14}H_{12}N_2Br_2S$	8.2	8.0
o-Me	139°	$C_{15}H_{15}N_2BrS$	9.7	9.6
m-Me	95°	,,	9.5	9.6
p-Me	157°	,,	9.8	9.6
o-OMe	145°	$C_{15}H_{15}ON_2BrS$	9.3	9.1
p-OMe	124°	,,	9.2	9.1

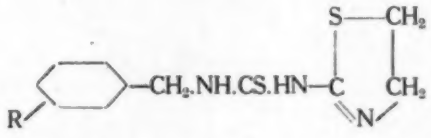
Compounds. (R=)	M.P.	Formula.	% Sulphur. Found.	Calc.
		X=*o*-Me.		
H	189°	$C_{15}H_{16}N_2S$	12.6	12.5
o-Cl	174°	$C_{15}H_{15}N_2ClS$	11.2	11.0
m-Cl	136°	,,	11.1	11.0
p-Cl	148°	,,	11.0	11.0
p-Br	166°	$C_{15}H_{15}N_2BrS$	9.7	9.6
o-Me	196°	$C_{16}H_{18}N_2S$	12.0	11.9
m-Me	140°	,,	11.7	11.9
p-Me	138°	,,	11.8	11.9
o-OMe	144°	$C_{16}H_{18}ON_2S$	11.3	11.2
p-OMe	160°	,,	11.1	11.2
		X=*p*-Me.		
H	131°	$C_{15}H_{16}N_2S$	12.7	12.5
o-Cl	114°	$C_{15}H_{15}N_2ClS$	11.2	11.0
m-Cl	120°	,,	10.9	11.0
p-Cl	174°	,,	11.1	11.0
p-Br	179°	$C_{15}H_{15}N_2BrS$	9.8	9.6
o-Me	107°	$C_{16}H_{18}N_2S$	12.0	11.9
m-Me	129°	,,	12.1	11.9
p-Me	124°	,,	11.8	11.9
o-OMe	129°	$C_{15}H_{15}ON_2S$	11.3	11.2
p-OMe	138°	,,	11.4	11.2
		X=2:5-Me_2.		
H	141°	$C_{16}H_{18}N_2S$	12.0	11.9
o-Cl	150°	$C_{16}H_{17}N_2ClS$	10.6	10.5
m-Cl	130°	,,	10.4	10.5
p-Cl	157°	,,	10.7	10.5
p-Br	152°	$C_{16}H_{17}N_2BrS$	9.3	9.2
o-Me	117°	$C_{17}H_{20}N_2S$	11.5	11.3
m-Me	99°	,,	11.4	11.3
p-Me	142°	,,	11.2	11.3
o-OMe	112°	$C_{17}H_{20}ON_2S$	10.8	10.7
p-OMe	137°	,,	10.9	10.7

TABLE II



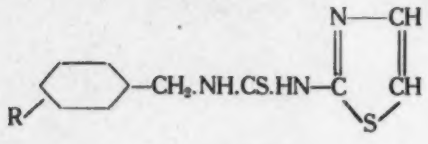
No.	Compounds. (R=)	M.P.	Formula.	% Sulphur. Found.	Calc.
1.	H	165°	$C_{13}H_{12}N_2S$	13.3	13.2
2.	*o*-Cl	174°	$C_{13}H_{11}N_2ClS$	11.6	11.5
3.	*m*-Cl	126°	$C_{13}H_{11}N_2ClS$	11.3	11.5
4.	*p*-Cl	179°	$C_{13}H_{11}N_2ClS$	11.7	11.5
5.	*o*-Br	186°	$C_{13}H_{11}N_2BrS$	10.1	10.0
6.	*m*-Br	128°	$C_{13}H_{11}N_2BrS$	9.9	10.0
7.	*p*-Br	176°	$C_{13}H_{11}N_2BrS$	10.2	10.0
8.	*o*-Me	174°	$C_{14}H_{14}N_2S$	12.7	12.5
9.	*m*-Me	97°	$C_{14}H_{14}N_2S$	12.4	12.5
10.	*p*-Me	184°	$C_{14}H_{14}N_2S$	12.6	12.5
11.	2:4-Me_2	167°	$C_{15}H_{16}N_2S$	11.9	11.8
12.	2:5-Me_2	158°	$C_{15}H_{16}N_2S$	12.0	11.8

TABLE III



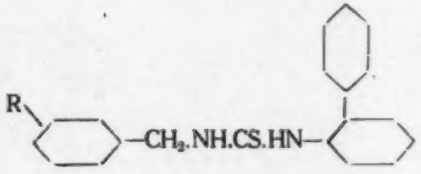
No.	Compounds. (R=)	M.P.	Formula.	% Sulphur. Found.	Calc.
1.	H	90°	$C_{11}H_{12}N_2S_2$	25.4	25.5
2.	*o*-Cl	115°	$C_{11}H_{11}N_2ClS_2$	22.6	22.4
3.	*p*-Cl	98°	,,	22.3	22.4
4.	*o*-Me	176°	$C_{12}H_{14}N_2S_2$	24.4	24.2
5.	*m*-Me	133°	,,	24.0	24.2
6.	*p*-Me	130°	,,	24.1	24.2
7.	3:4-Me_2	138°	$C_{13}H_{16}N_2S_2$	23.0	23.0
8.	2:4-Me_2	169°	,,	23.2	23.0
9.	2:5-Me_2	168°	,,	22.7	23.0

TABLE IV



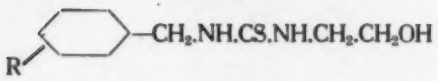
No.	Compounds. (R=)	M.P.	Formula.	% Sulphur. Found.	Calc.
1.	H	164°	$C_{11}H_{11}N_3S_2$	25.9	25.7
2.	o-Cl	195°	$C_{11}H_{10}N_3ClS_2$	22.4	22.6
3.	p-Cl	183°	,,	22.8	22.6
4.	p-Br.	179°	$C_{11}H_{10}N_3BrS_2$	19.7	19.5
5.	m-Me	127°	$C_{12}H_{13}N_3S_2$	24.5	24.3
6.	p-Me	155°	,,	24.2	24.3
7.	2:5-Me_2	174°	$C_{13}H_{15}N_3S_2$	23.3	23.1

TABLE V



No.	Compounds. (R=)	M.P.	Formula.	% Sulphur. Found.	Calc.
1.	H	112°	$C_{20}H_{18}N_2S$	10.2	10.1
2.	o-Cl	140°	$C_{20}H_{17}N_2ClS$	9.0	9.1
3.	m-Cl	195°	,,	9.3	9.1
4.	p-Cl	235°	,,	9.2	9.1
5.	o-Br	95°	$C_{20}H_{17}N_2BrS$	8.3	8.1
6.	o-Me	175°	$C_{21}H_{20}N_2S$	9.7	9.6
7.	3:4-Me_2	216°	$C_{22}H_{22}N_2S$	9.1	9.3
8.	2:4-Me_2	231°	,,	9.5	9.3
9.	2:5-Me_2	272°	,,	9.2	9.3

TABLE VI



No.	Compounds. (R=)	M.P.	Formula.	% Sulphur. Found.	Calc.
1.	o-Cl	110°	$C_{10}H_{13}ON_2ClS$	13.3	13.1
2.	p-Cl	211°	,,	13.0	13.1
3.	o-Me	112°	$C_{11}H_{16}ON_2S$	14.2	14.3
4.	2:4-Me_2	114°	$C_{12}H_{18}ON_2S$	13.7	13.5
5.	2:5-Me_2	135°	,,	13.4	13.5

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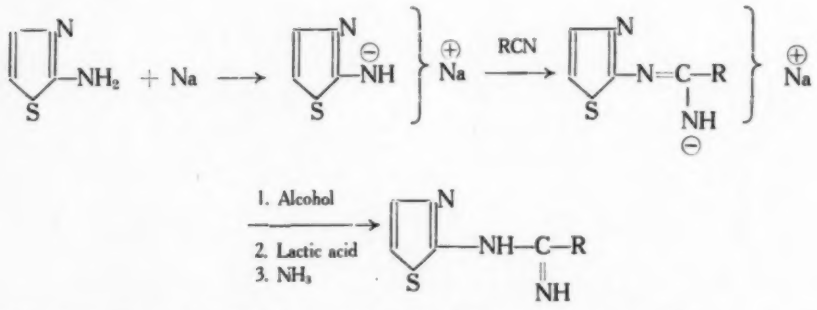
POSSIBLE ANTITUBERCULOUS COMPOUNDS. PART X. PREPARATION OF *N*-2-THIAZOLYL AND 6-BENZIMIDAZOLYL AMIDINES

BY VINAY S. MISRA AND MD. IMTIAZ HUSAIN

Several *N*-2-thiazolyl- and 6- benzimidazolyl-amidines have been synthesised with a view to studying their tuberculostatic activity.

The fact that many heterocyclic compounds like *N*-thiazolyl nicotinamide (*J. Org. Chem.*, 1948, **13,** 834), *iso*nicotinic acid hydrazide (Bernstein *et al.*, *Amer. Rev. Tuberc.*, 1952, **65,** 357) and *N*-4-phenyl-α-pyridyl-*p*-tolylamidine (Misra *et al.*, this *Journal*, 1954, **31,** 918) exhibit remarkable activity against *mycobacterium tubercule*, led the authors to prepare *N*-2-thiazolyl- and 6-benzimidazolyl-amidines. These amidines are expected to be highly active because of their strongly basic nature.

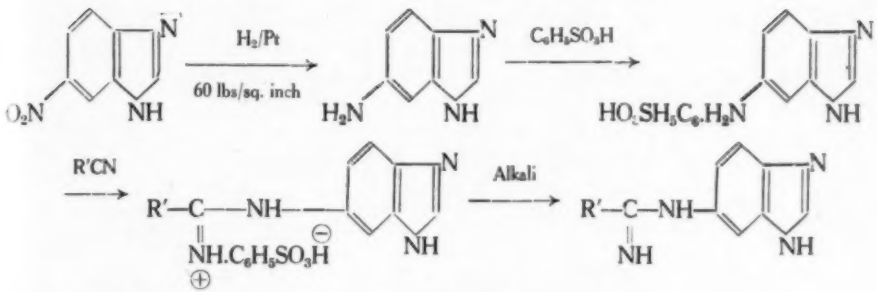
N-2-Thiazolylamidines were prepared by refluxing 2-aminothiazole, sodium, and the appropriate nitrile in dry benzene for 25 hours and then isolating the free amidines by the method of Cooper and Partridge (*J. Chem. Soc.*, 1953, 257). The possible mechanism of the reaction is as follows.



[R = Tol (*o*, *m*, & *p*), naphthyl (α and β), *p*-chlorophenyl and *p*-phenetoyl]

6-Aminobenzimidazole was obtained by reduction of 6-nitrobenzimidazole by means of hydrogen in the presence of Adams' catalyst; but being unstable, it was immediately converted into 6-benzimidazolylammonium benzenesulphonate. The formation of monosulphonate and not the disulphonate was confirmed by its nitrogen estimation.

The benzenesulphonate on fusion with an excess of (*o*, *m*, and *p*)-tolyl, naphtho (α and β), *p*-chlorobenzo and *p*-pheneto nitriles at 225-30° afforded the corresponding amidine benzenesulphonates after repeated trituration with acetone or ether. The amidine benzenesulphonates yielded free amidines by the usual process of basification and isolation.



[R' = Ph, Tol (*o*, *m* & *p*), naphthyl (α and β), *p*-chlorophenyl and *p*-phenetoyl]

The antitubercular activity of the amidines will be reported later on.

EXPERIMENTAL

N-2-*Thiazolylamidines*.—2-Aminothiazole (0.01 *M*), sodium (0.23 g.), and the nitrile (0.01 *M*) were refluxed in dry benzene (20 c.c.) in a 100 c.c. r.b. flask with a calcium chloride guard tube for 25 hours. Ethanol (5 c.c.) was added to dissolve any unchanged sodium as well as to decompose the sodio-amidine. The base after being converted into lactate was recovered by the addition of ammonia. The free amidines were recrystallised from acetone, ethanol or chloroform-petroleum ether.

TABLE I

N-2-*Thiazolylamidines*.

Amidine. (R=)	M.P.	% Yield.	Cryst. shape.	Cryst. from.	Formula.	% Nitrogen. Found.	Calc.
o-Tol	205-207°	58	Dark brown powder	Acetone	$C_{11}H_{11}N_3S$	18.90	19.35
m-Tol	133° (decomp.)	14	Brown powder	Chloroform.-pet. ether	$C_{11}H_{11}N_3S$	19.05	19.35
p-Tol	>280°.	7	Do	Acetone	$C_{11}H_{11}N_3S$	18.97	19.35
α-Naphthyl	177° (decomp.)	35	Do	Do	$C_{14}H_{11}N_2S$	16.94	16.60
β-Naphthyl	160°	32	Do	Ethanol	$C_{14}H_{11}N_3S$	16.23	16.60
p-Chloro-phenyl	118-19°	88	Brown shining crystals	Do	$C_{10}H_8N_3ClS$	18.00	17.60
Phenetoyl	>270°	17	Brown powder	Do	$C_{12}H_{13}ON_3S$	16.72	17.00

6-*Benzimidazolylammonium Benzenesulphonate* (A).—To 6-nitrobenzimidazole (9 g.), dissolved in dry dioxane (70 c.c.) at 50-60° in a hydrogenating bottle, Adams' catalyst (10 mg.) was added and the mixture shaken in an atmosphere of hydrogen at a pressure of 60 lbs. per sq. inch for 6 hours. The amine, so obtained in the solution being unstable, was immediately transferred to a 250 c.c. three-necked flask. Benzenesulphonic acid (1.5 g.), dissolved in dry methanol (5 c.c.), was added dropwise with stirring to this amine in solution. A white flocculent precipitate separated out; it was filtered, dried, and recrystallised from dioxane as a white amorphous powder, m.p. 232-33°, yield 98% (1.7 g.). (Found: N, 13.92. $C_{13}H_{13}O_3N_3S$ requires N, 14.4%).

6-Benzimidazolylamidines.—The above compound (A) was converted into different 6-benzimidazolylamidine benzenesulphonates and the latter into the corresponding free amidines by the method adopted by us previously (*loc. cit.*).

TABLE II

6-Benzimidazolylamidine benzenesulphonates.

Compound. (R′=)	M.P.	% Yield.	Cryst. shape (Powder).	Crystallised from.
Ph	224-26°	46	Brown	Acetone
o-Tol	210°	57	,,	,,
m-Tol	207°	50	Dark brown	,,
p-Tol	145° (decomp.)	57	Brown	,,
α-Naphthyl	136° (decomp.)	66	Black	Ether
β-Naphthyl	164-65°	86	Brown	Acetone
p-Chlorophenyl	201-202°	55	,,	,,
p-Phenetoyl	168-70°	13	,,	Ethanol

TABLE III

6-Benzimidazolylamidines.

Amidines. (R′=)	M.P.	% Yield.	Cryst. shape (Powder)	Formula.	% Nitrogen. Found.	Calc.
Ph*	>270°	13	Black	$C_{14}H_{12}N_4$	23.35	23.70
o-Tol*	>270°	30	,,	$C_{15}H_{14}N_4$	22.80	22.40
m-Tol**	183-84°	12	,,	$C_{15}H_{14}N_4$	22.90	22.40
p-Tol*	>275°	25	Dark brown	$C_{15}H_{14}N_4$	22.10	22.40
α-Naphthyl**	>270°	26	Black	$C_{18}H_{14}N_4$	19.17	19.58
β-Naphthyl*	202-203°	39	Grey	$C_{18}H_{14}N_4$	19.10	19.58
p-Chlorophenyl**	>270°	17	Dark brown	$C_{14}H_{11}N_4Cl$	20.25	20.70
p-phenetoyl*	>270°	39	Black	$C_{16}H_{16}ON_4$	19.70	20.00

* Crystallised from ethanol.
** ,, ,, chloroform—pet. ether.

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STABILITY OF METAL-CHELATE COMPOUNDS OF SOME VIOLURIC ACID DERIVATIVES

By R. P. Singh and N. R. Banerjee

Fe(II) forms deep blue complexes with violuric acid and its derivatives. A comparative study of the stabilities of the Fe(II) complexes with diphenylthiovioluric acid and the (*o*, *m* & *p*)-ditolylthiovioluric acids has been made by the spectrophotometric method. pK_a values of the three ligands have been determined by *p*H titrations against standard sodium hydroxide. It has been found that log *K* values of the chelates are related to pK_a values of the ligands. Introduction of the methyl group in the side benzene ring has been found to enhance the basic character of the ligands and also the stability of the metal chelates. The effect of the methyl group is most pronounced when it is situated in the *meta* position and is less when it is in the *para* position. Unexpectedly, the effect of methyl group has been found to be the least when it is present in the *ortho* position, and in this case steric factors seem to be involved.

Violuric acid derivatives have been found to form complexes with numerous metals by one of the authors (Singh, *Proc. Ind. Acad. Sci.*, 1946, **23A,** 330 ; this *Journal*, 1959, **36,** 57 ; 1960, **37,** 569 ; *J. Sci. Ind. Res.*, 1956, **15B,** 245). The group -CO-C(=NOH)-, contained in them, is analytically important since it confers upon the molecule the property of inner-complex salt formation. The chelates formed by ferrous iron with these reagents are deep blue in colour. The composition of the ferrous chelates corresponds to the formula FeX_2, in which X represents a substituted violuric acid anion. In view of the formation of chelates by all these reagents with Fe(II), it has been considered worth while to determine the stability constants of these complexes for ascertaining how the substituents in the violuric acid molecule affect the stability of the chelates.

Experimental

Diphenylthiovioluric acid and the three (*o*, *m*, and *p*)-ditolylthiovioluric acids were prepared by the methods described earlier (*loc. cit.*).

Determination of Stability Constants.—On account of the deep blue colour of the chelates formed by the reagents with ferrous iron, the spectrophotometric method was found to be convenient for determination of the stability constants. The use of this method requires a prior knowledge of the formula of the chelate under investigation. The formulas of the chelates studied were determined by analysis of the complexes thrown down as precipitates on the addition of the ammonium salt of the corresponding reagent to a saturated solution of a ferrous salt.

In the spectrophotometic method the optical density of the solution was used to determine the relative concentration of one of the components (usually the chelate) involved in the equilibrium. For the successful application of the method, only one substance should be coloured otherwise interference from other coloured substances must be avoided by applying a correction or by a close control of the wave length used. Further, Beer's law must hold for the coloured substance to be measured, which has been found to be the case for the systems investigated.

The stability constants of the ferrous chelates were determined by means of the following expression :

$$K = \frac{[MKe_2]}{[M] \times [Ke]^2}.$$

Optical density measurements of the chelates were carried out in presence of a large excess of the corresponding reagent in each case so that the formation of the chelates could be considered to be complete. It is necessary therefore that the reagent in excess does not have even a weak

absorption at the wave length used. The coloured chelates were found to possess maximum absorption at 660 mμ at which wave length the reagents did not show any absorption. Measurements of optical densities were then made at such reagent concentrations that the formation of chelates was incomplete. The concentrations of the chelates were calculated directly from Beer's law. This gave the value of MKe_2 in the equation. Knowing the value of MKe_2, the total quantity of Fe^{2+} present, and the total quantity of the chelating agent values of M and Ke could easily be determined; K was calculated in each case. The reagents being insoluble in water, optical density measurements were made in acetone-water mixtures. The proportion of acetone : water was maintained at 1 : 3 in all cases to facilitate comparison. The ionic strength of the solutions was maintained at a constant value by addition of potassium nitrate (0.2M) and as solutions of the reactants were very dilute, the activities of various constituents may be considered to remain unchanged and may be substituted by molar concentrations. To ensure the presence of iron completely in the ferrous state, a small quantity of hydroquinone was added before addition of the reagent. An excess of hydroquinone does not change the optical density of the system. The author had earlier found (this *Journal*, 1956, **33**, 335) that *p*H must be between 3.1 and 6.0 for maximum colour development. Consequently, *p*H of the solutions was maintained at 5.0 by using a buffer. Optical density measurements were made by using a spectrophotometer (Unicam, SP 600).

The following values of $\log_{10}K$ were calculated for the complexes of iron with different reagents :

Diphenylthiovioluric acid	$\log_{10}K=5.20$
Di-*o*-tolyl- „ „	$\log_{10}K=5.60$
Di-*p*-tolyl- „ „	$\log_{10}K=5.80$
Di-*m*-tolyl „ „	$\log_{10}K=6.08$

Each of the above values represents the mean of four values of $\log_{10}K$, determined from the results of measurement of optical densities of the solutions recorded in Tables I and II.

TABLE I

KNO_3=7 c.c. Buffer=7 c.c. Total volume=28 c.c.

Diphenylthiovioluric acid (0.05092 M) = y c.c. Fe^{2+}(0.000626M) = x c.c.			Di-*p*-tolylthiovioluric acid (0.02098 M) = y c.c. Fe^{2+}(0.001224M) = x c.c.		
Fe^{2+} soln.	Reagent.	O.D.	Fe^{2+} soln.	Reagent.	O.D.
6.8 c.c.	0.2 c.c.	0.022	2.0 c.c.	5.0 c.c.	0.590
2.0	5.0	0.220	6.5	0.5	0.130
6.8	0.2	0.020	2.0	5.0	0.585
2.0	5.0	0.200	6.5	0.5	0.129
6.8	0.2	0.021	2.0	5.0	0.580
2.0	5.0	0.210	6.5	0.5	0.128
6.8	0.2	0.020	2.0	5.0	0.590
2.0	5.0	0.210	6.5	0.5	0.131

TABLE II

KNO_3=7 c.c. Buffer=7 c.c. Total volume=28 c.c.

Di-*o*-tolylthiovioluric acid (0.02252 *M*) = *y* c.c. Fe^{2+}(0.001224 *M*) = *x* c.c.			Di-*m*-tolylthiovioluric acid (0.021636 *M*) = *y* c.c. Fe^{2+}(0.001224 *M*) = *x* c.c.		
Fe^{2+}soln.	Reagent.	O.D.	Fe^{2+}soln.	Reagent.	O.D.
2.0 c.c.	5.0 c.c.	0.540	2.0 c.c.	5.0 c.c.	0.633
6.5	0.5	0.070	6.5	0.5	0.231
2.0	5.0	0.550	2.0	5.0	0.625
6.5	0.5	0.072	6.5	0.5	0.227
2.0	5.0	0.545	2.0	5.0	0.630
6.5	0.5	0.071	6.5	0.5	0.230
2.0	5.0	0.540	2.0	5.0	0.640
6.5	0.5	0.070	6.5	0.5	0.235

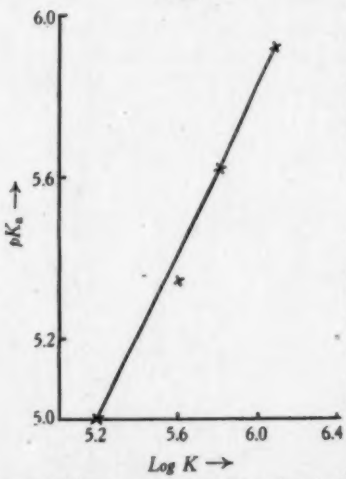
The pK_a values of the four reagents were determined by *p*H titrations in 50 : 50 dioxan-water mixture with a view to studying the relationship between the pK_a values and $\log_{10}K$ values of the ferrous complexes. The following pK_a values were obtained.

Diphenylthiovioluric acid = 5.00
Di-*o*-tolyl- „ „ = 5.35
Di-*p*-tolyl- „ „ = 5.60
Di-*m*-tolyl- „ „ = 5.90

DISCUSSION

The above pK_a values of the ligands are closely related to the $\log_{10}K$ values of the corresponding ferrous complexes; the order of pK_a values is the same as the order of stability constants of the corresponding ferrous complexes. There is a linear relationship between the two sets of values (Fig. 1).

FIG. 1



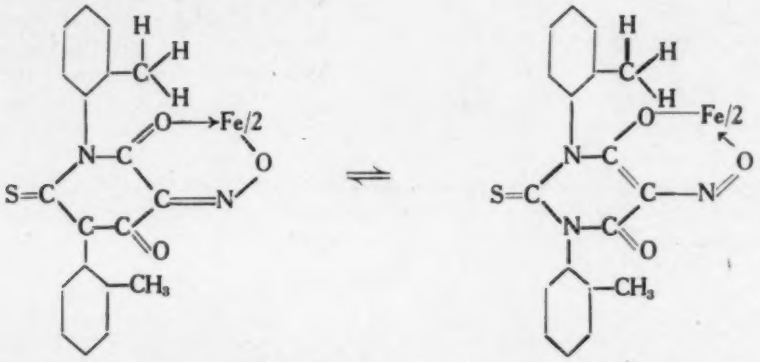
The increase in the basic strength of the ligands and also the stability of the ferrous complexes due to introduction of the methyl group in the side benzene ring appear to be explainable on the basis of the electron-releasing property of the methyl group.

The order of the basic strength of the three ditolylthiovioluric acids still remains to be explained. In this connection, it is interesting to note that Roberts (*J. Amer. Chem. Soc.*, 1951, **73,** 2181) found that the basic strength of substituted anilines was influenced to a greater extent when the substituent was present in the nearer *meta* position than in the more distant *para* position. Similar results were reported earlier by other workers (Kuhn and Zumstein, *Ber.*, 1926, **59,** 488; Pressman and Brown, *J. Amer. Chem. Soc.*, 1943, **65,** 540). It is therefore reasonable to suppose that the inductive effect of the methyl group would be experienced to a greater extent when the substituent is present in the *ortho* position, and would diminish when the methyl group is present in the *meta* position. The effect of the methyl group would

therefore be least when it is present in the *para* position on account of its greater distance from the reaction centre. In accordance with this view, di-*o*-tolylthiovioluric acid should be the strongest base and it should consequently furnish stablest complexes, while the basic strength of the *para* derivative should be the least.

The basic strength of di-*m*-tolylthiovioluric acid (pK_a=5.9) was found greater than that of the *para* compound (pK_a=5.6). This is according to expectations. But the basic strength of di-*o*-tolylthiovioluric acid and hence the stability of the corresponding complexes, which was expected to be greatest, was found to be the least (pK_a=5.35 ; $\log_{10}K$=5.60).

To explain the anomalous behaviour of di-*o*-tolylthiovioluric acid, the following resonating structures of the ferrous chelates are proposed.



In the above structures, due to the free rotation of the substituted benzene ring, the methyl group will not be able to pass the oxygen atom unless the chelate ring is distorted from its normal planar structure necessary for complete resonance. The distortion of the chelate ring would thus result in reducing the stabilising influence of resonance. This interpretation is supported by construction of molecular models. Alternatively, it is also likely that as a result of hyperconjugation, the C-atom of the methyl group attached to the benzene nucleus will become somewhat negative and one of its hydrogen atoms would then become positive due to no-bond resonance. The latter will then tend to form a hydrogen bond with the oxygen atom of the adjacent carbonyl group, reducing its co-ordinating capacity.

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DECOMPOSITION OF HYDROGEN PEROXIDE BY HYDRATED CERIC OXIDE

By D. R. Nabe and B. P. Gyani*

The rate of decomposition of aqueous hydrogen peroxide (0.350 to 0.022*M*) in presence of freshly precipitated ceric oxide (0.0031 to 0.0250 molar proportions) in the temperature range 25-40° has been followed by the gas collection method. The first order k is steady at first, but shows a decreased value at later stages. The apparent energies of activation are low (about 12000 cal./mole). The value of k falls as the oxide is gradually dehydrated by heating at a number of selected constant temperatures (complete loss of activity at about 730°).

The results have been explained on the assumption that the basic mechanism is provided by the Michaelis-Menten equation for enzymatic decompositions, but the adsorbed molecule does not decompose unless hit by another H_2O_2 molecule from the solution phase. There does not seem to be any complication due to free radical chains.

Although the decomposition of hydrogen peroxide in aqueous solutions has been studied in presence of a number of metallic oxides (Fe_2O_3, CuO, H_2O, etc.), ceric oxide does not appear to have received much attention. Lemoine (*Compt. rend.*, 1916, **162,** 702) reported that the oxide was a moderately good catalyst at 69.6° with 30 volumes hydrogen peroxide. In this work we have investigated the decomposition in some detail.

Experimental

The hydrogen peroxide was a commercial sample and contained some stabiliser. No attempt was made to purify it so that the rate of self-decomposition could be kept low. Ceric oxide was precipitated from ceric nitrate by dilute ammonium hydroxide and washed without loss of any solid. The moist oxide was kept stored under distilled water, and known weights were withdrawn after making up the mixture to a definite volume in a measuring flask. The amount of oxide was computed from the initially taken weight of ceric nitrate. It was found that if the suspensions were thoroughly shaken before withdrawal, the weight of oxide removed by means of a pipette did not vary by more than 1.2%.

Since the residual hydrogen peroxide cannot be titrated with potassium permanganate in presence of the oxide, the rate was followed by collecting the oxygen evolved in a nitrometer tube. The mixture was kept vigorously stirred on a magnetic stirrer.

Variation of Rate with Increasing Concentration of Hydrogen Peroxide

In the first series of experiments the proportion of ceric oxide (hydrated) was kept constant at 0.025 mole/litre and that of hydrogen peroxide was changed in different experiments, which were performed at 35° (thermostat 35° ± 0.1°). The initial first order k_1's with increase in initial concentration of H_2O_2 are recorded in Table I.

TABLE I

Conc. of CeO_2 = 0.025 mole/litre.

Initial conc.	1st order k_1.	Remarks.
(a) 0.3500 mole/litre	0.0067	1st order reaction
(b) 0.2500	0.0129	Do
(c) 0.1750	0.0304	Do
(d) 0.0875	0.0783	Departs from 1st order at low conc.
(e) 0.0435	0.1244	Do
(f) 0.0325	0.1312	Do
(g) 0.0218	0.0967	Do

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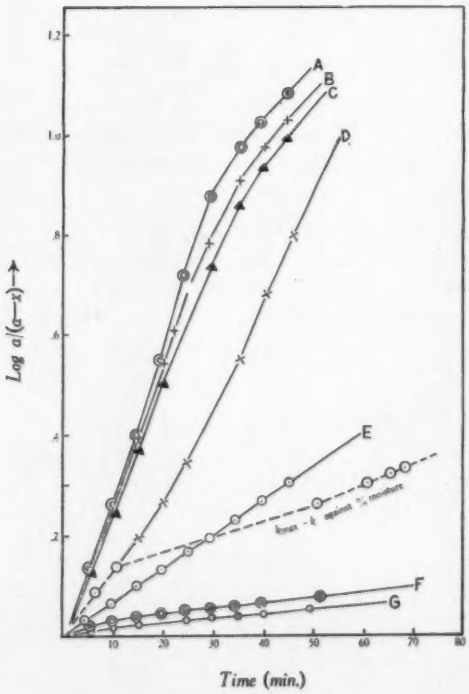
The reaction was found to be of 1st order throughout the course of decomposition, observed only in the first three cases. The velocity constant (1st order) showed a decrease as the decomposition progressed, *i.e.*, as concentration of H_2O_2 decreased in the system. This departure set in earlier, the smaller the starting concentrations, and did so at log $a/(a-x)=0.45$ approximately in (f), *i.e.*, at about 40% of 0.0325 molar H_2O_2 still undecomposed.

Variations of the Amount of Oxide

The above experiments do not make it clear whether a decreased absolute concentration of H_2O_2 in the system produces a departure from the 1st order reaction. The question remains open that a critical ratio of $(H_2O_2)/(CeO_2)$ may be responsible. Hence another set of experiments was performed in which the (H_2O_2) was kept constant at 0.0325*M* and the amount of (CeO_2) was increased from 0.00313 to 0.025 mole/litre. Whereas straight line graphs were obtained [log $a/(a-x)$ against t] for oxide "concentrations" 0.00313 and 0.0062, the 0.025 graph showed strong departure (towards lower values of k) as the (H_2O_2) in the system decreased to about 40% of its initial value (0.013*M*∼). The ratio $(H_2O_2)/(CeO_2)$ is about 0.55 at this point, but perhaps this might have set in even at a lower $(H_2O_2)/(CeO_2)$ ratio since the margin between 0.0062 and 0.025 for the oxide is large. An analysis of the data leading to Table I showed that in some cases a ratio as low as 0.45 produced a departure from the 1st order. The graphs of log $a/(a-x)$ against t, where a downward bending occurs, are typical of reactions where a 1st order eventually changes to a 2nd order. We presume therefore that the reactions are of 1st order to start with, but at lower concentrations of perioxide they change to 2nd order.

FIG. 1



Apparent Energy of Activation

Obviously in involved reactions like these, it is not possible to calculate the true energy of activation, but assuming the reactions to be of 1st order, the apparent energy has been calculated from velocity constants determined at different temperatures (25°-40°) for two mixtures: (*i*)0.0325*M* H_2O_2—0.025*M* CeO_2; (*ii*) 0.0325*M* H_2O_2—0.0125*M* CeO_2. A straight line graph was obtained only in (*ii*) (where the proportions of oxide was less), when log k was plotted against $1/T$ and the apparent E_a was 12560 cal./mole, having quite a low value. The other graph had a larger slope at smaller $1/T$, but the mean slope was again about 12000 cal./mole. It may be concluded that the reacting molecules easily acquire the necessary energy of activation.

DISCUSSION

It will appear from the above that these reactions are characterised by (*i*) a first order rate at a high H_2O_2/CeO_2 ratio, (*ii*) a tendency towards second order when the oxide is in excess, and (*iii*) a low energy of activation. These facts bring out a strong similarity with enzymatic decomposition, studied in detail by Michaelis and Menten (*Biochem. Z.*, 1913, **49**, 333). If the peroxide=P and the catalyst=C, we may write down,

$$P + C \underset{K_1}{\overset{K_2}{\rightleftharpoons}} PC \xrightarrow{K_1} O_2 + H_2O.$$

PC may be regarded as a temporary complex between the peroxide and the catalyst; the end products are of course oxygen and water, and are formed by a first order mechanism (velocity constant $= k_1$). PC is formed by a second order mechanism (velocity constant $= k_2$), but part of it may be dissociated back into P and C by a first order mechanism (velocity const.$=k_{-1}$)

$$\frac{d(PC)}{dt} = k_2 (P)(C) - (k_{-1} + k_1)(PC) \quad .. \quad (i)$$

Also
$$\frac{d(O_2)}{dt} = k_1 (PC) \quad .. \quad (ii)$$

It will be noted that the concentration of the catalyst is not quite fixed, $= (C)_\circ$, but will depend on how much PC has been formed.

$$(C) = (C)_\circ - (PC).$$

Hence from (*i*)

$$\frac{d(PC)}{dt} = k_2 \{(C_\circ) - (PC)\}(P) - (k_{-1} + k_1)(PC) \quad .. \quad (iii)$$

since (P) — (PC) is almost equal to (P), there being far more peroxide molecules than catalyst sites. If a steady state is permitted,

$$\frac{d(PC)}{dt} = 0.$$

Hence from (*iii*),

$$(PC)\{k_2 (P) + k_{-1} + k_1\} = k_2 (C)_\circ (P)$$

or
$$(PC) = \frac{k_2 (C)_\circ (P)}{k_2 (P) + k_{-1} + k_1}.$$

Substituting the values of (PC) in (*ii*),

$$\frac{d(O_2)}{dt} = \frac{k_1 . k_2 (C)_\circ (P)}{k_2 (P) + (k_{-1} + k_1)} \quad .. \quad (iv)$$

Equation (*iv*) requires that at high concentrations of hydrogen peroxide [when k_2 (P) will be large compared to $k_{-1} + k_1$], the evolution of oxygen should be of zero order with respect to concentrations of hydrogen peroxide, but at low concentrations it should be of the first order. Actually we have seen that the reaction is of the first order at high concentrations of H_2O_2 and tends to second order at lower concentrations, a $(H_2O_2)/(CeO_2)$ ratio of about 0.5 being necessary at lower concentrations of H_2O_2 with the samples of moist oxide prepared by us. At high concentrations of peroxide, the lowest concentrations reached at the end of the actual experiments are still considerable, and equation (*iv*) must be modified.

How are we to account for the missing order both at low and high concentrations of H_2O_2? It appears that the adsorption complex PC is not able to break down spontaneously into the products H_2O, O_2

$$C{-}H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2 + C.$$

The complex must be hit by another H_2O_2 from the solution phase before oxygen can appear as a gas. Hence the reaction may be written :

$$C{-}H_2O_2 + H_2O_2 \longrightarrow 2H_2O + O_2 + C.$$

Such a mechanism has been previously suggested by Hinshelwood and Allen (*Proc. Roy. Soc.*, 1928, **121A,** 141) for the decomposition of CH_3CHO on various metal surfaces.

Since this mechanism depends on the formation of the complex PC, it is obvious that the physical conditions of the oxide may be of great significance. In the last series of experiments we subjected the moist oxide to successive desiccation at increasing temperatures. The velocity constants obtained with these dried samples showed a progressive decrease as the moisture content decreased. Up to 400° the decrease in k is not very great, but above this it is very rapid because sudden dehydration takes place near this temperature and the structure of ceric oxide changes towards fluorite structure as reported by Moosath (*J. Inorg. Nucl. Chem.*, 1959, **2,** 286). It changes to complete fluorite structure at 900°. There was a total loss of catalysis with the sample dried at 730° for 2 hours. The results are shown in Table II and the corresponding kinetic data are shown in Fig. 1.

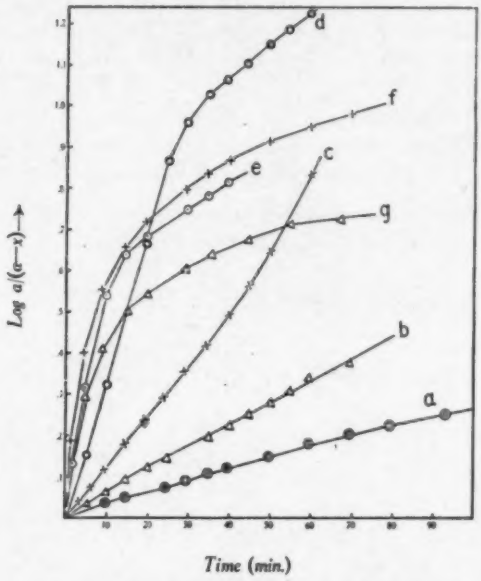
TABLE II

		%Loss.	k_{t_1}.	$k_{max}-k$.
A—	heated at 110° to const. wt.		6066	..
B—	125°/2 hrs.	0.20	0.063	0.003
C—	175°/2	0.40	0.057	0.009
D—	225°/2	2.17	0.037	0.029
E—	430°/2	10.40	0.015	0.051
F—	530°/2	12.07	0.044	0.062
G—	630°/2	13.09	0.0028	0.063
H—	730°/2	13.49	0.00	0.066
I—	830°/2	13.73	0.00	0.066

The graph of the 1st order k against %moisture lost (calculated on the basis of sample A) is also inserted in Fig. 1. Actually $k_{max}-k$ has been plotted against %moisture lost. Obviously there is a simple relation between $k_{max}-k_2$ and moisture lost. The graph recalls the Langmuir adsorption equation and suggests that the water molecules adsorped in favourable positions in the oxide structure may be the seat of catalysis. Obviously the moisture is not regained by the catalysts B, C, etc., when the oxide is immersed in the reaction mixtures, or in any case it is not bound in the same manner as in A. This raises the question whether some of the bound moisture in A may not be lost as a consequence of long immersion in H_2O_2 so that the nature of the catalyst may not be quite the same throughout a single run. The slight fall eventually observed in k_1 even in the best cases may be explained in this manner. To see this point further, we allowed a freshly prepared sample of oxide to react with H_2O_2 (0.107 g. oxide to 25 c.c. of 0.0325*M*-H_2O_2)

till no further O_2 was evolved. The oxide was then transferred without loss to another H_2O_2 solution of the same volume and concentration. The k_1 now observed was found to be only 50% of the former.

FIG. 2



We also examined the X-ray diagrams of four of the samples recorded in Table II. We did not find any considerable change in the reflected X-ray diagram of the oxide due to heating and moisture loss. The water molecules may well be located in interstitial spaces. It appears that the adsorption complexes must also be formed through the agency of these water molecules and that hydrogen bonding or simply physical forces may be involved.

It may be further noted that the rate of stirring is of no consequence so long it is fairly vigorous. A mixture could be left unstirred during the beginning of a run, and stirred only before reading the volume of gas collected, with errors no larger than 2%. On the other hand, in the decomposition of hydrogen peroxide, catalysed by ammonium molybdate-sodium nitrate mixtures (to be communicated later), even small differences in the rate of stirring had a profound effect on the volume of gas collected. We therefore conclude that stirring in the present experiments is necessary only for releasing the supersaturation of the reaction mixture by evolved oxygen, no complications such as free radical chains being involved.

Further work is in progress. The authors thank Prof. M. N. Verma of the Department of Physics, Patna University for the X-ray photographs.

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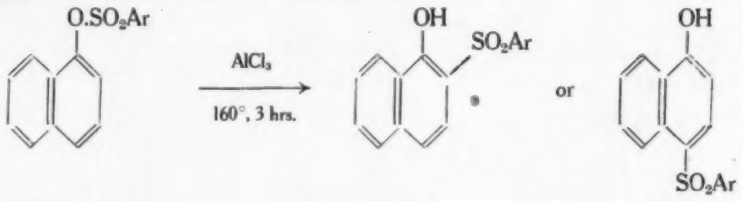
SOME ARYL NAPHTHYL SULPHIDES AND SULPHONES

BY V. BALASUBRAMANIYAN AND V. BALIAH

The Fries isomerisation of α-naphthyl benzene-, *p*-toluene- and *o*-toluene-sulphonates is described. The resulting sulphones are shown to be *o*-hydroxysulphones from their ultraviolet absorption spectra as well as wet and dry melting points. Methyl α-naphthyl ether condenses with arenesulphonyl chlorides in the presence of anhydrous stannic chloride to furnish aryl 4-methoxynaphthyl sulphones.

In a recent publication (this *Journal*, 1959, **36,** 391), we reported the isomerisation of sulphonates derived from β-naphthol. In the present communication the results of the isomerisation of α-naphthyl benzene-, *o*-toluene- and *p*-toluene-sulphonates are presented.

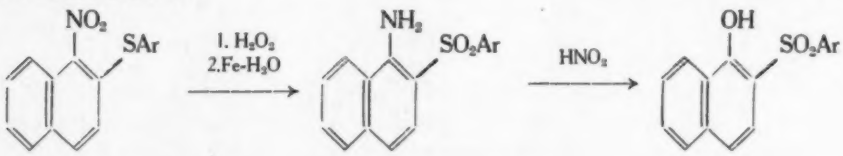
The sulphonates (I) on treatment with anhydrous aluminium chloride at 160° for three hours underwent rearrangement to afford small amounts of alkali-soluble products. In each case only one hydroxysulphone could be isolated from the reaction mixture. The product can be *o*-hydroxysulphone (II) or *p*-hydroxysulphone (III).



(I) (II) (III)

[Ar = Ph, *p*-Tol or *o*-Tol]

To establish the identity of the Fries product, the *o*- and *p*-isomers were sought to be synthesised by unambiguous methods. For the synthesis of the *o*-hydroxysulphones (II), the following scheme was attempted. The conversion of the aminosulphone to the hydroxy compound was, however, not successful.



[Ar = Ph, *o*-Tol or *p*-Tol]

The *p*-hydroxysulphones were easily obtained by the Friedel-Crafts reaction of methyl α-naphthyl ether with arenesulphonyl chlorides (cf. Leandri and Maioli, *Ann. chim.*, 1955, **45,** 3; *Chem. Abs.*, 1955, **49,** 15785) and by subsequent demethylation of the products. The identity of the sulphones thus obtained was established by condensing 1-bromo-4-methoxynaphthalene with appropriate thiophenols and oxidising the resulting sulphides. The demethylated sulphones were found to be different from those obtained by the Fries isomerisation of α-naphthyl arenesulphonates. This ruled out the possibility of the Fries products being *p*-hydroxysulphones.

That the Fries products are *o*-hydroxysulphones was also borne out by a consideration of their wet and dry melting points. The depression in melting point, when wet, is large for asso-

ciated compounds while it is small for chelated molecules. Amstutz *et al.* (*Science*, 1950, **111**, 305) have indeed employed this method to show that chelation exists in *o*-hydroxysulphones.

FIG. 1

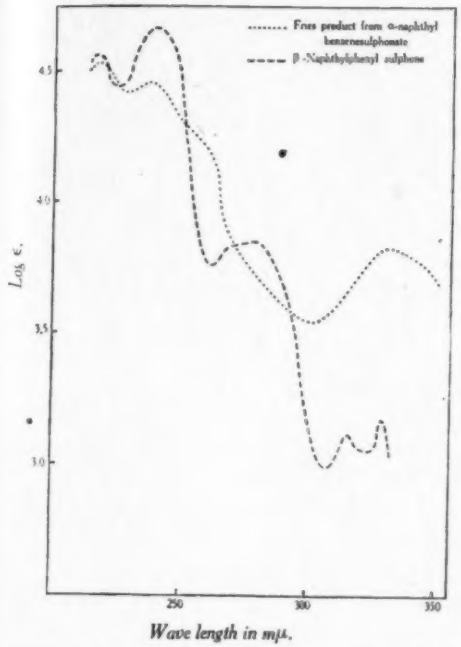


FIG. 2

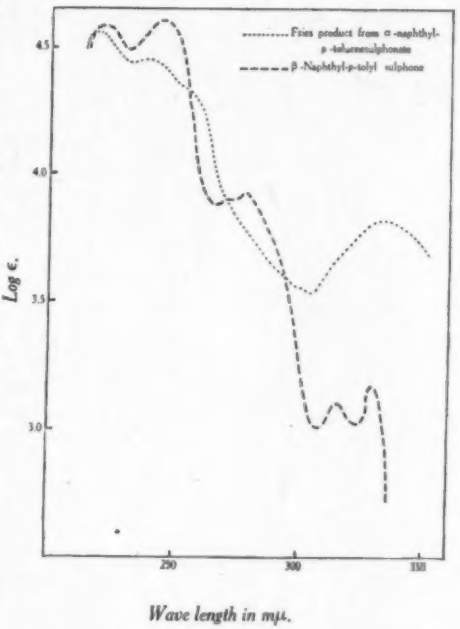


Table I shows the differences in the dry and wet melting points of the sulphones obtained by the isomerisation of α-naphthyl sulphonates. For comparison, the differences in the dry and wet melting points of the synthetic *p*-hydroxysulphones are also shown. The data clearly indicate that the Fries products are *o*-hydroxysulphones.

TABLE I

Compound.	Dry m.p.	Wet m.p.	Diff.
Fries product from α-naphthyl benzenesulphonate	132°	126°	6°
Fries product from α-naphthyl *o*-toluenesulphonate	119°	114°	5°
Fries product from α-naphthyl *p*-toluenesulphonate	134°	129°	5°
1-Hydroxy-4-naphthyl phenyl sulphone	170°	112°	58°
1-Hydroxy-4-naphthyl *o*-tolyl sulphone	168°	111°	57°
1-Hydroxy-4-naphthyl *p*-tolyl sulphone	129°	97°	32°

The ultraviolet spectral data (Table II) also lead to the same conclusion. In diphenyl sulphone, the principal absorption band is at 235 mμ (ϵ_{max} 17,400). In *o*-hydroxydiphenyl sulphone this band undergoes a slight hypsochromic shift with decrease in the intensity of absorption (λ_{max} 233 mμ, ϵ_{max} 12,600). In *p*-hydroxydiphenyl sulphone there is a bathochromic shift

of this band (λ_{max} 256 mμ, ϵ_{max} 16,000). A similar behaviour is seen with the naphthalene derivatives listed in Table II (see also Figs. 1-4). If it is assumed that the Fries products are *o*-hydroxysulphones, their absorption spectra exhibit a hypsochromic shift, when compared to the absorption spectra of the parent sulphones (β-naphthyl phenyl sulphone and β-naphthyl *p*-tolyl sulphone). On the other hand, the spectra of the *p*-hydroxysulphones may be seen to exhibit a bathochromic shift, when compared to the spectra of the parent sulphones (α-naphthyl phenyl sulphone and α-naphthyl *p*-tolyl sulphone).

FIG. 3

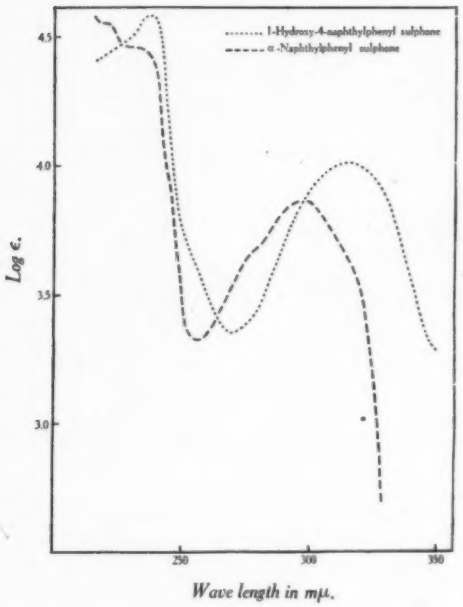


FIG. 4

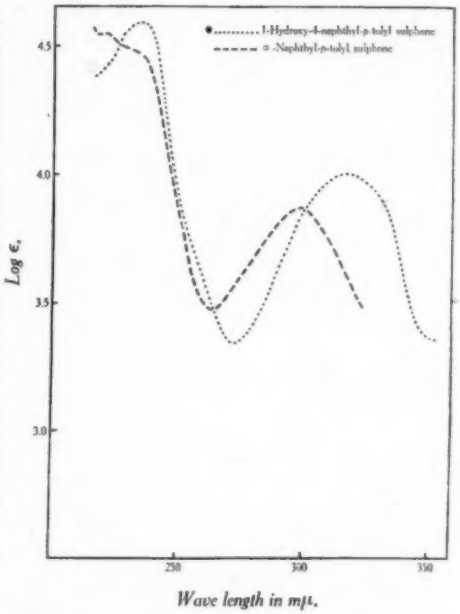


TABLE II

(Spectra in 95% ethanol)

Compound.	*$\lambda_{max.}$	$\epsilon_{max.}$
β-Naphthyl phenyl sulphone	240 mμ	46,000
	218	36,000
Fries product from α-naphthyl benzenesulphonate	237	29,000
	218	34,100
β-Naphthyl *p*-tolyl sulphone	244	39,400
	222	37,400
Fries product from α-naphthyl *p*-toluenesulphonate	239	27,700
	220	35,700
α-Naphthyl phenyl sulphone	231	28,300
	219	35,000
1-Hydroxy-4-naphthyl phenyl sulphone	236	37,600
α-Naphthyl *p*-tolyl sulphone	†(232)	30,200
	†(220)	34,400
1-Hydroxy-4-naphthyl *p*-tolyl sulphone	235	37,800

* Only the high intensity bands are given.

† Shoulders are shown in parentheses.

EXPERIMENTAL

α-Naphthyl o-toluenesulphonate was obtained by treatment of α-naphthol with *o*-toluenesulphonyl chloride in the presence of ethanolic KOH. It crystallised from ethanol as needles, m.p. 115-16°. (Found : C, 68.34 ; H, 4.53. $C_{17}H_{14}O_3S$ requires C, 68.45 ; H, 4.73%).

Fries Rearrangement of α-Naphthyl Sulphonates.—The procedure adopted was the same as reported earlier (*loc. cit.*). The sulphonates, which were isomerised, and the products obtained are indicated in Table III. In ethanolic solution, the hydroxysulphones exhibit a green colour with ferric chloride.

TABLE III

Sulphonate.	%Yield.	Formula.	Hydroxysulphone. M.P.	%Carbon. Found.	%Carbon. Calc.	%Hydrogen. Found.	%Hydrogen. Calc.
α-Naphthyl benzene-	12	$C_{16}H_{12}O_3S$	131-32°	67.36	67.62	4.71	4.22
α-Naphthyl *p*-toluene-	10	$C_{17}H_{14}O_3S$	133-34°	68.39	68.45	5.00	4.73
α-Naphthyl *o*-toluene-	2	$C_{17}H_{14}O_3S$	118-19°	68.21	68.45	4.57	4.73

1-Amino-2-naphthylphenyl Sulphone.—1-Nitro-2-naphthyl phenyl sulphone (5 g.) (Neumoyer and Amstutz, *J. Amer. Chem. Soc.*, 1944, **66**, 1680) was suspended in water (100 c.c.). Iron filings (10 g.) and ferrous sulphate (5 g.) were added to the above, the mixture refluxed for 90 minutes, and poured into water. The solid residue was extracted with ethanol, when, pale yellow needles separated (4.3 g.). It was repeatedly crystallised from ethanol in needles, m.p. 144-45°. The above reduction was not successful with tin and HCl (conc.).

2-Chloro-1-nitronaphthalene was condensed with *p*-thiocresol and *o*-thiocresol. The nitrosulphides obtained were oxidised to the nitrosulphones with H_2O_2 and then reduced to the aminosulphones. The relevant data regarding these compounds are shown in Table IV.

TABLE IV

Compound.	%Yield.	Formula.	M.P.	%Carbon. Found.	%Carbon. Calc.	%Hydrogen. Found.	%Hydrogen. Calc.
1-Nitro-2-naphthylphenyl S*	90	$C_{16}H_{11}O_2NS$	59°(a)	..	..	..	..
1-Nitro-2-naphthyl phenyl S'*	100	$C_{16}H_{11}O_4NS$	149°(b)	..	..	..	..
1-Amino-2-naphthyl phenyl S'	86	$C_{16}H_{13}O_2NS$	144-45°(a)	67.78	67.84	4.80	4.60
1-Nitro-2-naphthyl *p*-tolyl S*	80	$C_{17}H_{13}O_2NS$	105°(a)	..	..	..	..
1-Nitro-2-naphthyl *p*-tolyl S'	100	$C_{17}H_{13}O_4NS$	173°(b)	62.70	62.37	3.77	4.00
1-Amino-2-naphthyl *p*-tolyl S'	60	$C_{17}H_{15}O_2NS$	164-65°(a)	68.63	68.66	5.16	5.09
1-Nitro-2-naphthyl *o*-tolyl S	85	$C_{17}H_{13}O_2NS$	123°(a)	69.34	69.13	4.65	4.44
1-Nitro-2-naphthyl *o*-tolyl S'	100	$C_{17}H_{13}O_4NS$	127-28°(b)	62.50	62.37	4.19	4.00
1-Amino-2-naphthyl *o*-tolyl S'	90	$C_{17}H_{15}O_2NS$	134-135(a)	68.77	68.66	5.08	5.09

N.B. S and S' denote respectively sulphide and sulphone.
(a) Crystallised from ethanol, (b) crystallised from acetic acid.
* Neumoyer and Amstutz, *loc. cit.*

4-Methoxy-1-naphthylphenyl Sulphide.—To dry sodium phenyl sulphide (obtained from 0.8 g. of sodium and 3.7 g. of thiophenol) were added 4-bromo-1-methoxynaphthalene (8 g.) (Szmuzcovicz and Modest, *J. Amer. Chem. Soc.*, 1950, **72**, 566) and copper powder (0.5 g.). The mixture was heated at 220-40° for 4 hours. The reaction mixture was then steam-distilled after adding

zinc dust (2 g.) and H_2SO_4 (1 : 1 ; 25 c.c.). The semisolid residue was extracted with ethanol and recrystallised from the same solvent in pale white crystals, m.p. 87-88°, yield 77%. (Found : C, 75.97 ; H, 5.22. Calc. for $C_{17}H_{14}OS$: C, 76.67 ; H, 5.30%). Leandri and Maioli (*loc. cit.*) report m.p. 72°.

4-*Methoxy*-1-*naphthylphenyl Sulphone.*—Oxidation of the above sulphide in acetic acid with excess of 5% $KMnO_4$ solution furnished the sulphone. On crystallisation from acetic acid, it melted at 194-95°. (Found : C, 67.66 ; H, 4.45. Calc. for $C_{17}H_{14}O_3S$: C, 68.42 ; H, 4.73%).

4-*Hydroxy*-1-*naphthylphenyl Sulphone.*—The foregoing compound (1 g.) was demethylated by refluxing with hydriodic acid (*d* 1.7 ; 10 c.c.) at 170-80° for 4 hours. The reaction mixture was poured into water, the solid obtained was washed with water, and digested with a 10% solution of NaOH. The alkali extract on acidification furnished the hydroxysulphone in 60% yield. It crystallised from ethanol as colorless plates, m.p. 169-70°. (Found : C, 67.57 ; H, 4.26. $C_{16}H_{12}O_3S$ requires C, 67.57 ; H, 4.64%). It develops a green colour with ferric chloride.

Friedel-Crafts' Reaction of Methyl α-Naphthyl Ether with p-*Toluenesulphonyl Chloride.*—From methyl α-naphthyl ether (5.3 g.) and *p*-toluenesulphonyl chloride (6.5 g.) and using anhydrous stannic chloride as catalyst, the methoxysulphone was obtained in 60% yield. The compound crystallised from acetic acid as tiny plates, m.p. 203-204°, not depressed by an admixture with a synthetic sample of 4-methoxy-1-naphthyl *p*-tolyl sulphone. (Found : C, 69.45 ; H, 5.56. $C_{18}H_{16}O_3S$ requires C, 69.20 ; H, 5.16%).

4-*Methoxy*-1-*naphthyl*-p-*tolyl sulphide* was prepared in 60% yield from 4-bromo-1-methoxynaphthalene (8 g.) and dry sodium *p*-tolyl sulphide (5 g.). Repeated recrystallisation from ethanol gave fine, colorless needles, m.p. 102-103°. (Found : C, 76.67 ; H, 6.37. $C_{18}H_{16}OS$ requires C, 77.13 ; H, 5.75%).

4-*Methoxy*-1-*naphthyl*-p-*tolyl Sulphone.*—Oxidation of the above sulphide with aqueous $KMnO_4$ furnished the sulphone in 60% yield. It crystallised as flat needles from acetic acid, m.p. 202-204°. (Found : C, 68.92 ; H, 4.92. $C_{18}H_{16}O_3S$ requires C, 69.20 ; H, 5.16%).

4-*Hydroxy*-1-*naphthyl*-p-*tolyl Sulphone.*—Demethylation of the foregoing methoxysulphone with hydriodic acid in the usual way gave the hydroxysulphone in 60% yield. It crystallised from ethanol as fine needles, m.p. 128-29°. (Found : C, 68.98 ; H, 4.83. $C_{17}H_{14}O_3S$ requires C, 68.45 ; H, 4.73%). It exhibits a green colour with ferric chloride.

Friedel-Crafts' Reaction of Methyl α-Naphthyl Ether with o-Toluenesulphonyl Chloride.—Methyl α-naphthyl ether (5.3 g.) and *o*-toluenesulphonyl chloride (6.5 g.) gave the methoxy sulphone in 60% yield (6 g.). Two crystallisations from acetic acid gave fine, colorless needles, m.p. 195-96°. (Found : C, 69.52 ; H, 5.10. $C_{18}H_{16}O_3S$ requires C, 69.20 ; H, 5.16%).

4-*Hydroxy*-1-*naphthyl*-o-*tolyl Sulphone.*—Demethylation of the above sulphone furnished the hydroxysulphone in 60% yield. It crystallised as shining plates from aqueous ethanol, m.p. 167-68°. (Found : C, 68.16 ; H, 4.64. $C_{17}H_{14}O_3S$ requires C, 68.45 ; H, 4.73%). It shows a green colour with ferric chloride.

Ultraviolet Absorption Measurements.—The spectra were determined using a Beckman quartz spectrophotometer, Model DU. The solvent used was 95% ethanol.

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SPECTROPHOTOMETERIC STUDIES OF CARMINIC ACID COMPLEXES

By Trilok Chand Jain

Carminic acid complexes with Cu^{2+}, Pb^{2+}, Th^{4+}, and Zr^{4+} have been studied spectrophotometerically, when these (including carmic acid) are present in comparable low concentrations of 10^{-4} mole/litre at room temperature. While copper and lead form stable complexes in water and acid solutions, the complexes and the acid are unstable in alkaline solutions. Thorium probably forms a salt but not a complex, and zirconium does not appear to react under these conditions.

The capacity of carminic acid to form a complex with many different cations has been studied by many workers (Welcher, "Organic Anal. Reagents", Vol. IV, p. 443, D. Van Nostranad Publication, 1955). Carminic acid contains the same reactive groups as other hydroxyquinone dyes. Since it contains in addition a carboxyl group, which may function as a part of reactive structure, it has been thought proper to study its complexing properties under acid, neutral, and alkaline conditions.

Experimental

Complexes of Cu^{2+}, Pb^{2+}, Th^{4+}, and Zr^{4+} were studied spectrophotometerically. Carminic acid in water solution has a deep red colour and is yellow to violet in acid solutions. The absorption spectra are shown in Figs. 1 and 2. In alkaline medium, the colour obtained immediately is deep purple, which fades on standing. λ_{max} and the associated molecular extinction coefficients for carminic acid are recorded in Table I.

Table I

Medium.	λ_{max}.	pH.	ϵ.	Colour.
Water	500	3.4	6,800	Stable
HCl 2×10^{-2}	490-500	2.0	5,800	,,
NaOH 1×10^{-4}	540	6.2	3,450	Unstable
NH_4Cl 1×10^{-3}	540	..	7,800	,,

Fig. 1

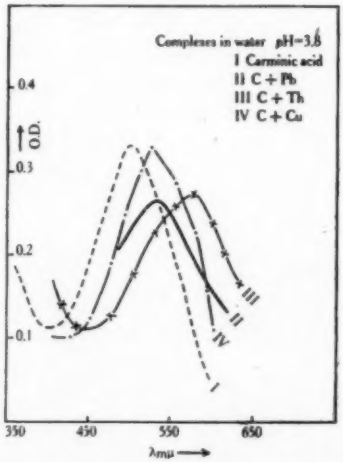
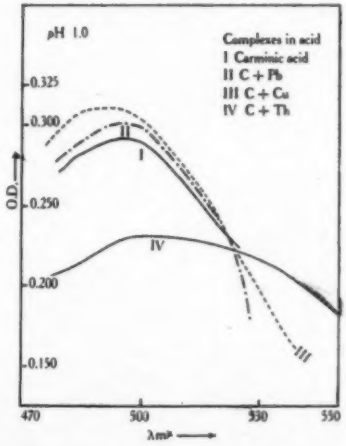


Fig. 2



Solutions of analytical grades of $CuSO_4$, $Pb(NO_3)_2$, $Th(NO_3)_4$, and technical grade of zirconium nitrate and BDH carminic acid were prepared by dissolving the appropriate amounts in

water to get the concentrated solution and diluting them to furnish the concentrations in the range of 10^{-4} mole/litre. Bausch and Lomb Spectronic 20 colorimeter was used for measurements of optical densities with 1 cm cuvettes.

Nature of Complexes.—For a set of experiments, mixtures containing varying concentrations of metallic ions and carminic acid, either in water or in HCl or NaOH, were prepared and the optical density in each case was measured in the range of 400-600 mμ. The absorption spectra in water and HCl are reproduced in Figs. 1 and 2. In the presence of alkalies, wherever the colour was unstable, optical densities immediafely after mixing were noted and compared (Table II).

TABLE II

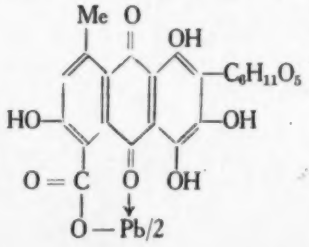
Carminic acid $= 1 \times 10^{-4}$ mole/litre $= C$.

Ratio C : M.	$\lambda_{max.}$	O.D.	Remarks.
	M = Copper sulphate.		
1:1	535 mμ	0.355	NaOH × 10^{-3}. Colour purple, unstable
1:0.6	540	0.355	NaOH × 10^{-3}. Colour purple, unstable
	M = Thorium nitrate		
1:1	570	0. 320	NaOH × 10^{-3}. Blue, stable
	M = Lead nitrate.		
1:1	545	0. 423	NaOH × 10^{-3}. Blue-purple, unstable

Finally Job's method (*Ann. chim.*, 1928 *x*, **9**, 113) of continued variation was also applied to ascertain the molar composition of the metallic complexes.

DISCUSSION

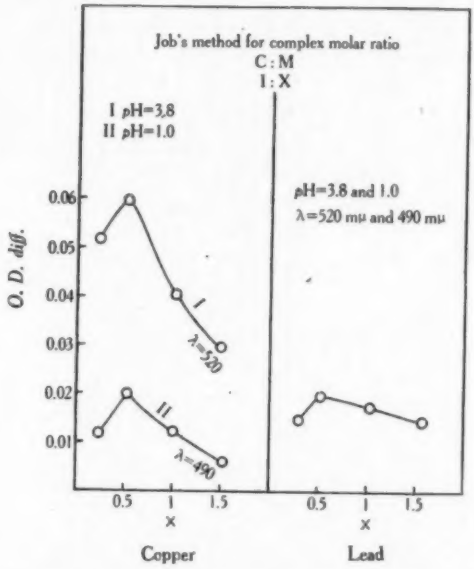
From Figs. 1 and 2 it would be seen that copper and lead form complexes in water as in HCl. The increasing acidity has very slight effect on the absorption of complexes. The molar ratios for the complexes would appear to be 1 of carminic acid to 0.5 of the metal at *p*H 1.0 to 3.8 by using Job's method (Fig. 3). From Figs. 1 and 2 it would appear that the maximum absorption wave length for the complexes and for the acid alone are practically the same, but these differ in their molar absorbance index. After making an allowance for the free acid absorbance, the optical densities at the maximum absorbance wave lengths for the complexes were plotted against the increasing concentrations of the metal ions (Fig. 3) to obtain the composition ratio of the complexes. The molar ratio for lead complex has been reported to be the same by Pavelka (cf. Welcher, *loc. cit.*), and the probable structure as given to the complex is as shown below.



(I)

Pb^{2+}, Cu^{2+}, and Th^{4+} are reported to form purple precipitates, which dissolve on addition of HCl ("Reagents for Qualitative Inorganic Analysis", edited by Wengar and Duckert, Elsevier Publishing Co., 1948, p. 150).

FIG. 3



The effect of alkalies on the colour of the complexes is of particular interest. It has been noticed that the colour of copper and lead complexes disappears on their addition. The stronger the alkalies, quicker is the fading, which is also the case when only carminic acid is taken. The colour of the thorium solution, however, was found to remain unaffected by addition of alkalies even when other cations were present. But the absorption maxima shift with the changing concentrations of thorium (Table III) when the concentration of carminic acid and pH (6.2) are kept the same.

TABLE III

Th conc. $\times 10^{-4}$ ..	0.19	0.12	0.06	0.251	0.503	0.603	1.02	1.52	2.29
λ_{max} (mμ) ..	550	510	510	560	570	570	570	575	580

Now this difference of the behaviour of thorium cation on the one hand and of copper or lead cations on the other leads us to believe that lead and copper form complexes, structures of which would be like the one shown elsewhere, and that while reaction with thorium would be different, it does not form a complex but probably forms a salt with carminic acid. The thorium salt of carminic acid remains stable in presence of alkalies while the copper and lead complexes are unstable in their presence. The fading of colour of carminic acid alone (10^{-4} mole/litre) with NaOH (10^{-3} mole/litre) could be followed spectrophotometerically at room temperature. Average value on the first order reaction constant k was found to be 6.8×10^{-3} mole per min. Similarly the kinetics of the copper complex colour fading, under identical conditions, provide the value of the first order constant $k = 1.5\times10^{-2}$ mole min^{-1}. It would thus appear that the mechanism for

these would be the same. In the case of thorium, if it forms a true salt and not a co-ordinated complex, it will remain unaffected on addition of alkalies as both the oxygen atoms of the two carbonyl groups are not co-ordinated; the colour might however, disappear if excess of alkali is used so that thorium hydroxide so obtained may absorb the dye as was found by Goto (*Chem. Abs.*, 1941, **35,** 1720) in case of cochineal, which contains a high percentage of carminic acid.

Mixtures of Cations.—When a mixture of copper and thorium is taken, the O.D. measurements show that absorption is entirely due to copper complex; thorium does not interfere at all pH ranges.

Reaction with Zirconium.—Although reported as a spot test by Feigl ("Spot Test", p. 157, 1947) the reaction with zirconium at such low concentrations of carminic acid does not appear to take place in any medium at room temperature.

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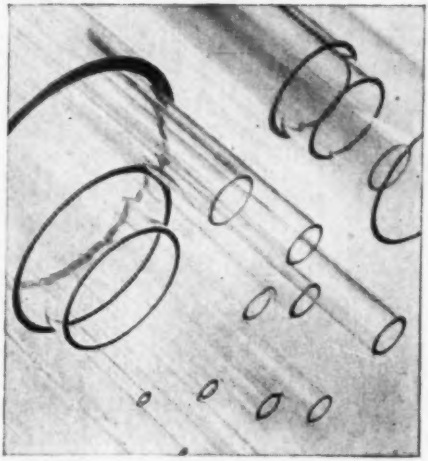

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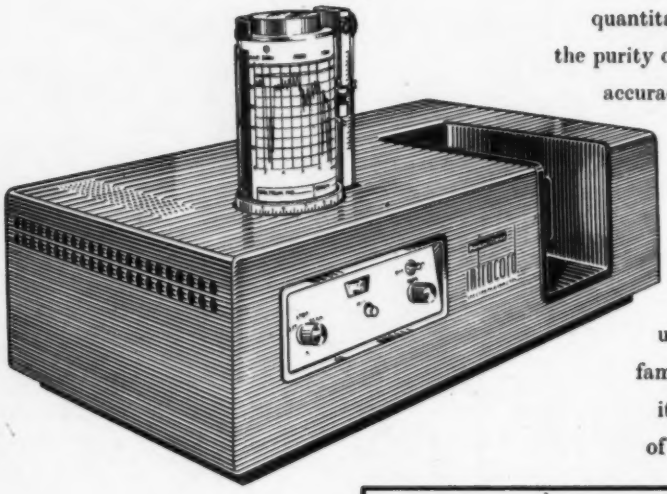

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